Preparation and Characterization of Activated Carbon from Tire and Biomass Char and its Applications in Liquid Phase Adsorption

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Certificate

This is to certify that thesis entitled "*Preparation and Characterization of Activated Carbon from Tire and Biomass and It Applications in Liquid-Phase Adsorption*", being submitted by Mr. A.V.S.L.Sai Bharadwaj (Roll No: 612CH3003) has been carried out under my guidance in partial fulfillment of requirement for the degree of Masters of Technology (Research) in department of chemical engineering, National Institute of Technology-Rourkela and this work has not been submitted elsewhere for a degree.

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A.V.S.L.Sai Bharadwaj

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Nomenclature:

Q_e	Adsorption Capacity (mg/gm)
C_o	Initial Concentration (mg/lit)
C_e	Equilibrium Concentration (mg/lit)
K, a	Langmuir constants
R	Dimensionless separation factor
K_f	Freundlich constant
1/n	heterogeneity factor

Abbreviations:

AC	Activated Carbon
CS	Castor Seed
PAC	Powdered Activated Carbon
GAC	Granular Activated Carbon
ACF	Activated Carbon Fibers
CAC	Commercial Activated Carbon
TAC	Tire Derived Activated Carbon
BAC	Biomass Derived Activated Carbon
RHC	Rice Husk Carbon

Abstract

Waste tyre and biomass (castor seed (CS)) char has been selected as precursor for the production of activated carbon (AC) in the present investigation. Activated carbon is prepared through chemical activation method by using potassium hydroxide (KOH) as the activating agent in the temperature range of 300°C-700°C for an activation time of 30minutes in a tubular furnace. The effects of activation temperature on yield% and surface area of activated carbon were studied. Characterization of activated carbon by nitrogen adsorption at 77K was utilized to determine the specific surface area of these carbon samples, we observed that the surface area of the carbon samples increases with the activation temperature and reaches to a maximum. Fourier Transform Infrared spectroscopic analysis (FTIR) was performed in order to determine the functional groups present in the activated carbon prepared. The surface morphology of the activated carbon samples was analyzed by Scanning Electron Microscope (SEM). Activated carbons offer a potential tool for methylene blue adsorption in aqueous phase. Adsorption studies of methylene blue on the prepared activated carbons were carried out at optimum conditions. To obtain details of methylene blue on activated carbon UV-visible spectroscopic analysis was employed at 660nm. The effect of major variables such as effect of contact time, pH, and adsorbent dosage were investigated. The adsorption equilibrium data was well explained by Langmuir and Freundlich isotherm. The adsorption capacity of methylene blue on activated carbon prepared from tyre and biomass char was compared with the adsorption capacity of methylene blue on commercial available activated carbon and rice husk carbon. It was found that the adsorption capacity of methylene blue on commercial available activated carbon and rice husk carbon is low when compared to activated carbon derived from precursor.

Chapter-1

Introduction

1.1 Role of Activated Carbon (AC):

Activated carbon (AC) has been widely used as adsorbents for the removal of contaminating organic compounds in treatment of water and waste water. AC prepared from various naturally occurring carbonaceous materials, such as coal, wood, coconut shell, and other polymer wastes are used in water purification, air purification, and also in batteries and fuel cells. Commercially available ACs derived from carbonaceous raw materials such as various ranks of coal (lignite, bituminous coal, and anthracite) are relatively expensive and their manufacturing processes require elaborate activation procedures to generate well defined surface properties. In such circumstances the economics involved in their use are unfavorable. From various research works it has been reported that ACs can also be obtained from municipal and industrial wastes such as polyethylene terephthalene (PET) waste and refuse derived fuel (RDF). AC demand will benefit from a continuing intensification of the global environmental movement as well as rapid industrialization. In most developing and developed countries, the use of ACs in pharmaceutical sector offers the strongest growth prospect. Additionally, environmental concerns in developing regions will spur new growth in water treatment applications, which is already the largest single market in developed countries. Besides the necessity of clean drinking water, government environmental regulations that vary by region also impact the demand for AC in this sector significantly. The high adsorption capacities of ACs are related to properties such as surface area, pore volume and pore size distribution (PSD). These unique characteristics depend on the type of raw materials employed for preparation of AC and the method of activation.

Various research works indicates that there have been many attempts to obtain low-cost ACs from agricultural wastes such as coconut shells [1,2], wood [3,4],rice husk [5,6], olive seeds [7],sugar cane bagasse [8] etc. Although, a variety of raw materials were explored for the preparation of AC in earlier studies, scientists are still trying to explore new materials depending on their availability and suitability for AC production.

Basically there are two different processes for the preparation of AC: physical activation and chemical activation. Physical activation involves carbonization of carbonaceous material followed by the activation of the resulting char at high temperatures (800°C – 1100°C) in the presence of oxidizing agents such as CO_2 and steam. In chemical activation the precursor is mixed with a chemical agent and then pyrolysed at low temperatures (400°C – 600°C) in the absence of air. Chemical activation offers several advantages over physical activation as it is

carried out in a- single step process, lower activation temperature(<800°C) giving higher yields in less activation time and therefore resulting in the development of a better porous structure[9].

In the present study waste tire and biomass (castor seed) chars are employed as precursor for the preparation of AC by chemical activation method. Due to the increasing demand of AC, there is a strong need for sorting out new precursors for the preparation of AC which should be cost effective and compare with the commercially available AC. Most of the previous studies on the preparation of AC from waste tires and biomass chars concerned the porosity development during the activation as well as the applications of carbon in liquid-phase adsorption. When tires are no longer usable, they are usually dumped in landfill sites, or burned in cement kilns [10,11]. Biomass is the biological material from living organism mostly referring to flora of the ecosystem which refers to plants and generally plant derived materials. The main source of biomass generally comes from the forestry products, agriculture crops and residues and biological wastes. Since biomass are renewable source of energy they can be used directly or indirectly when once they are converted into useful products.

1.2 Methylene Blue:

The efficiency of ACs prepared by various chemical activations in the removal of Methylene blue from aqueous phase solution has been investigated in this study. Methylene blue is a heterocyclic aromatic chemical compound with chemical formula $C_{16}H_{18}N_3SCl$. It has many uses in a range of different fields, such as biology and chemistry. At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water. Methylene blue is a monoamine oxidase inhibitor (MAOI) [12], and if infused intravenously at doses exceeding 5 mg/kg, may precipitate serious serotonin toxicity, serotonin syndrome, if combined with any selective serotonin reuptake inhibitors (SSRIs) or other serotonin reuptake inhibitor (e.g., duloxetine, sibutramine, venlafaxine, clomipramine,imipramine) [13]. Methylene blue causes many side effects to human health affecting various parts such as cardio vascular muscles (hypertension, precordial pain), central nervous system (dizziness, mental confusion, headache, fever), dermatologic (staining of skin, injection of site necrosis), gastrointestinal (fecal discoloration, nausea, vomiting, abdominal pain), genitourinary (discoloration of urine, bladder irritation), hematologic (anemia).[14]. Adsorption of methylene blue from the aqueous phase is a useful toll for product control of adsorbents. The most commonly used methods for removal of

methylene blue are biological oxidation and chemical precipitation. However, these processes are effective and economic only in cases where contamination concentrations are relatively high. Currently sorption process is proved to be one of the effective and attractive processes for the treatment of wastewaters [15]. Also this method will become inexpensive, if the sorbent material used is inexpensive and does not require any expensive additional pretreatment step. The major advantages of an adsorption system for water pollution control are less investment in terms of initial cost, simple design and easy operation, less energy intensiveness, non-toxic, and superior removal of organic waste constituents as compared to the conventional biological treatment processes [15].

1.3 **Problem Statement:**

Methylene blue is one of the contaminants of waste water coming out from many dye industries. Recent research works focused on the development of cost effective alternatives using various natural sources and industrial wastes. The use of low cost agricultural materials, waste and residues for recovering heavy metals and dyes from contaminated industrial effluent has merged as a potential alternative method to high cost adsorbents. Most of the research works refers to production of ACs from waste tire and biomass char. Production of AC from waste tire and biomass char has generated considerable interest.

The disposal of tires represents a major environmental issue throughout the world like tire stock piles provide breeding ground for mosquitoes, in turn causing serious diseases affecting human health. Biomass is biological material from living, or recently living organisms, most often referring to plants or plant-derived materials. ACs prepared from tire and biomass char have been used to adsorb methylene blue, phenols, basic dyes, and also for removal of heavy metals from waste water.

1.4 Objectives:

The overall objective of this work is to prepare AC (AC) from waste tire and biomass (castor seed mixed with different catalysts) for the efficient removal of methylene blue from aqueous phase.

The specific objectives of this study are:

- To prepare AC from waste tire char and biomass char by chemical activation method using KOH as the chemical activating agent.
- To estimate the effect of activation temperature on the yield% and surface area of the AC prepared.
- To study and compare the characteristics of developed AC with commercially available AC.
- To remove methylene blue from aqueous phase by ACs prepared at optimum conditions and to determine the effect of various process parameters such as effect of pH, effect of adsorbent dose, effect of contact time on removal of efficiency of AC.

1.5 Scope of Study:

This study shall provide a better solution to methylene blue pollution in aqueous phase by developing an efficient microporous adsorbent. It will also provide an ideal technology to utilize and convert waste tire and biomass char into a valuable product i.e. AC which can be commercialized for the removal of contaminants from aqueous phase.

1.6 Organization of Thesis:

The thesis has been organized into six chapters:

Chapter-1: Introductory chapter

Chapter-2: Contains the detailed literature review on various topics related to the present work

Chapter-3: Includes all the materials and methods involved in the work

Chapter-4: Contains the result and discussions of the experimental work carried out.

Chapter-5: Contains the conclusions and future perspective.

Chapter 2

Literature Review

2.0 Summary:

This chapter gives a detailed review on the pertinent literature on preparation of AC and its applications in liquid-phase adsorption. It provides a thorough input on the history, types, characterization and utilization related to AC. It also demonstrates about the effect of various parameters which influence the Methylene blue adsorption on AC.

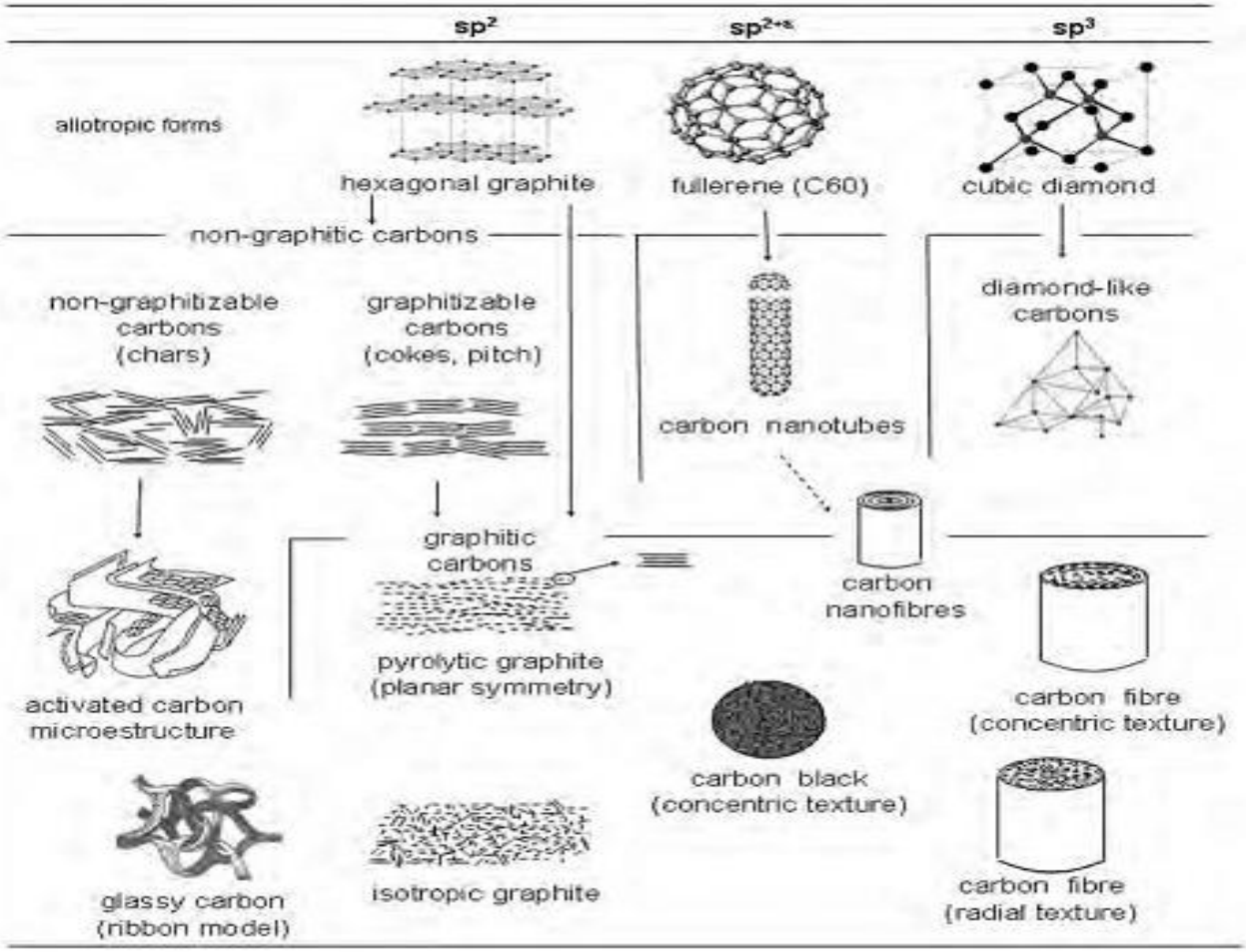
2.1 Types of Carbon Materials:

Carbon is the chemical element with symbol C and atomic number 6; it is non metallic and tetravalent making four electrons to form covalent chemical bonds. All the carbon materials composed of the carbon element has unique bonding with other elements and with itself. Depending on the type of hybridization of carbon atoms, the main allotropic forms of carbon are classified as graphite, diamond, and fullerene.

Graphite is an amorphous form of carbon atom which is in a non-crystalline, irregular, glassy state but not held in macro structure. It is present as a powder, and is the main constituent of substances such as charcoal, lampblack (soot), and AC. Graphite has a hexagonal layered structure (sp^2-based structure) in which carbon atoms are bonded to neighboring carbon atoms $sp^2\sigma$ and delocalized π bonds. The allotropic forms of carbon are classified into graphitic and non-graphitic carbons respectively. Non-graphitic carbons in turn are classified into graphitizable and non-graphitizable carbons. At very high pressures carbon forms the more compact allotrope Diamond, having nearly twice the density of graphite. Diamond forms a cubic 3D-structure (sp^3-based structure) in which each carbon atom is bonded with four other carbon atoms through $sp^3\sigma$ bonds. Diamond has the same cubic structure as silicon and germanium and because of the strength of carbon-carbon bonds, it is the hardest naturally occurring substance in terms of resistance and scratching. Fullerenes have a graphite-like structure but instead of purely hexagonal packing, they2 contain pentagons of carbon atoms, which blend the sheet into spheres, ellipses, or cylinders. Fullerenes are three dimensional carbon structures where the bonds between the carbon atoms are bent to form an empty cage of sixty (C_{60}) or more carbon atoms. [16] .The properties of fullerenes have not yet been fully analyzed and represent an intense area of research in nonmaterial.

Carbons exhibit different structures depending on the size and such a wide variety of possible structures gives rise to a large amount of different types of carbons.

Figure-2.1 Schematic representation of major allotropic forms of carbon and some carbon structures derived from these forms.



2.2 Activated Carbon (AC):

Activated carbon (AC) is a non-graphitic, non-graphitizable carbon with a highly disordered microstructure. It is also called as activated charcoal, activated coal, or carboactivatus. AC is well known for its high adsorption capacity due to its high surface area.

2.2.1 Historical Background:

AC is mostly used in gas purification, decaffeination, and gold purification, metal extraction, water purification, sewage treatment, as medicine, as air filters in gas masks and respirators, as filters in compressed air and has many other applications.

Table- 2.1 Applications of AC in various fields and its uses:

S.No	Applications	Uses
1	Medical uses	To treat poisonings and over doses following oral ingestion
2	Analytical chemistry applications	In 50% w/w combination with celite, is used as stationary phase in low pressure chromatographic separation of carbohydrates (mono, di-trisaccharides) using ethanol solution (5-50%) as mobile phase in analytical or preparative protocols
3	Environmental applications	Spill cleanup, Ground water remediation, Drinking water filtration, Air purification, Volatile organic compounds capture from painting, dry cleaning, gasoline dispensing operations, and other processes.
4	Fuel storage	To store natural gas and hydrogen gas.
5	Gas purification	To remove oil vapors, odors, and other hydrocarbons from air.
6	Chemical purification	To purify solutions containing un-wanted colored impurities such as during a recrystallization procedure in organic chemistry
7	Distilled alcoholic beverage purification	AC filters can be used to filter vodka and whisky of organic impurities which can affect color, taste and odor
8	Mercury scrubbing	ACs often impregnated with sulphur or iodine is widely used to trap mercury emissions from coal-fired power stations, medical incinerators, and from natural gas at the wellhead.

2.2.2 Preparation of AC:

Basically there are two different processes for the preparation of AC: physical activation and chemical activation. Physical activation involves carbonization of carbonaceous material followed by the activation of the resulting char at high temperatures (800 – 1100 °C) in the presence of oxidizing agents such as CO_2 and steam. In chemical activation the precursor is mixed with a chemical agent and then pyrolysed at low temperatures (400 – 600 °C) in the absence of air. Chemical activation offers several advantages over physical activation as it is carried out in a, Single step process, Lower activation temperature (<800°c), Higher yields, Less activation time and therefore resulting in the development of a better porous structure [9]. Typical preparation of AC involves carbonization of raw material in the absence of oxygen, and activation of carbonized product [18].

2.2.2.1 Physical Activation:

Physical activation is a two step process, which involves carbonization of raw material followed by activation at elevated temperatures in the presence of suitable oxidising gases such as carbon dioxide, steam, air or their mixtures. Carbonization temperature ranges between 400°C-800°C, and the activation temperature ranges between 800°C-1100°C.

Table-2.2 Various physical activating agents and precursors used for AC production:

S.No	Activating agent	Material	Reference
1	Steam	Rice husk, corn cob, olive residues, sunflower shells, pinecone, rapeseed, cotton residues, olive-waste cakes, coal, rubber wood sawdust, fly ash, coffee endocarp, tire	Ariyadejwanich Petal., (15),Abdel-Nasser Aetal.,(18), Artal Setal.,(19), Zhe Luetal., (20), Pedro Netal.,(21), Velan Metal.,(22), Yang Zetal.,(23), Cunliffe A.Metal.,(24), Allen J.Letal.,(25), Brady T.Aetal.,(26), Rood M.Jetal.,(27)
2	CO_2	Oak, corn hulls, coconut shells, corn Stover, rice straw, rice hulls, pecan shells, pistachio nutshells, coffee	Pedro Netal.,(21), Aworn Aetal.,(28), Ramon Metal.,(29), Wei Letal.,(30), Yang Tetal.,(31), Salvador Fetal.,(32),

		endocarp, sugarcane bagasse, corn cob, waste tires, textile fibres, anthracite, tire	Helleur Retal.,(33), Chi Yetal.,(34), Miguel G.Setal.,(35), Teng Hetal.,(36).
3	Air	Peanut hulls, almond shells, olive tree	Sabio Eetal, (37), El-Hendawyetal. (38), Sahu J.Netal, (39).

2.2.2.2: Chemical Activation:

Preparation of AC by chemical activation is a single step process in which carbonization and activation is carried out simultaneously. Initially the precursor is mixed with a chemical activating agent, which acts as dehydrating agent and oxidant. Chemical activation offers several advantages over physical activation which mainly include (i) lower activation temperature (<800°C) compared to physical activation temperature (800°C-1100°C), (ii) single activation step, (iii) higher yields, (iv) short activation time. The most commonly used chemical activating agents are H_3PO_4, $ZNCl_2$, and KOH.

Table-2.3 Various chemical activating agents and precursors used for AC production:

S.No	Activating agent	Material	Reference
1	$ZNCl_2$	Corn cob, coconut shells, macadamia, nutshells, peanut hulls, almond shells, hazelnut shells, apricot stones, rice husk, tamarind wood, cattle-manure, pistachio-nut shells, bagasse, sunflower seed hulls.	Araujo J.C.Setal.,(1), Chetty Ketal.,(8), Ahmadpour Aetal.,(9), Yang Tetal.,(31), El-Hendawyetal.,(38), Sahu J.Netal., (39), Tzong-Horng L(40), Motoi Metal.,(41), Acharya Jetal.,(42).
2	KOH	Rice straw, corn cob, macadamia nutshells, peanut hulls, olive seed, rice straw, cassava peel, petroleum coke, coal, cotton stalk, pine apple peel.	Basta A.Hetal.,(5), Stavropoulos G.Getal.,(7),Ahmadpour Aetal.,(9), Teng Hetal.,(36), Tang Jetal.,(43), Hameed B.Hetal.,(44), Oh G.Hetal.,(45), Fujio Wetal.,(46), Feng-Chin Wetal.,(47), Ru-Ling Tetal.,(48).

3	H_3PO_4	Hemp, Peanut hulls, almond shells, pecan shells, corn cob, bagasse, sunflower seed hulls, lignin, grain sorghum, rice straw, oak, birch, sewage sludge, chestnut wood, eucalyptus bark, rice hull, cotton stalk, jackfruit peel.	Grazyna Getal.,(3), Liu Jetal.,(4), Guo Yetal.,(6), Tzong-Horng L(40), Fan L.Tetal.,(49), El-Hendawyetal.,(38), Muniz Getal.,(50), Daniel Metal.,(51), Prasert Petal.,(52), Prahas Detal.,(53), Bedia Jetal.,(54)

2.2.3: Classification of Activated Carbon:

ACs are complex products and the classification is difficult based on their preparation methods, physical properties, and surface characteristics. However, the general classification of ACs based on particle size divides them into Powered AC (PAC), Granular AC (GAC), and AC Fibers (ACF).

2.2.3.1: *Powered AC (PAC)*:

Powered AC (PAC), has a typical particle size of less than 0.1 mm and the common size of the particle ranges from 0.015 to 0.025 mm. Typical applications of PAC are industrial and municipal waste water treatments, sugar decolourization, in food industry, pharmaceutical, and mercury and dioxin removal from a flue gas stream [44, 55, 56, 57, 58].

2.2.3.2: *Granular AC (GAC)*:

Granular AC (GAC) has a mean particle size between 0.6 to 4 mm. It is usually used in continuous processes of both liquid and gas phase applications. GAC has an advantage over PAC, of offering a lower pressure drop along with the fact that it can be regenerated and therefore reused more than once. In addition to the proper micropore size distribution, its high apparent density, high hardness, and a low abrasion index makes GAC more suitable over PAC for various applications [59, 60, 61, 62, 63].

2.2.3.3: *AC Fibers (ACF)*:

AC Fibers (ACFs) are carbonized carbons which are subsequently heat treated in an oxidizing atmosphere. ACF began to be developed in 1970 using the precursor viscose rayon which mainly consists of cellulose. Later thermo set polymer materials like saran and phenolic resins were used as precursors to produce ACF. A good ACF precursor must be non-graphitic and nongraphitizable carbon fibre which was isotropic in nature. From the end of 1980s, interest

is still centred on the production of ACFs from various inexpensive precursors [54, 64, 65, 66, 67].

2.2.4: Methylene Blue:

Methylene blue is a heterocyclic aromatic chemical compound with chemical formula $C_{16}H_{18}N_3SCl$. At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water and is widely applicable to biological and chemical fields. Methylene blue is a monoamine oxidase inhibitor (MAOI) [12] and when infused intravenously at dosage of 5mg/kg and combined with any selective serotonin reuptake inhibitors (SRRIs) or other serotonin reuptake inhibitor (e.g., duloxetine, sibutramine, venlafaxine, clomipramine, and imipramine) it may be precipitated to serious serotonin toxicity, serotonin syndrome [13]. Methylene blue causes many side effects to human health such as cardio vascular (hypertension, precordial pain), central nervous system (dizziness, mental confusion, headache, fever), dermatologic (staining of skin, injection of site necrosis), gastrointestinal (facial discoloration, nausea, vomiting, abdominal pain), genitourinary (discoloration of urine, bladder irritation), hematologic (anemia) [14].

2.2.4.1: Removal of Methylene Blue by AC from Aqueous-Phase:

Among the numerous adsorbents available, AC is the most popular and widely used for the removal of methylene blue from aqueous phase. Adsorption of methylene blue from the aqueous phase is a useful tool for product control of adsorbents. The most commonly used methods for removal of methylene blue are biological oxidation and chemical precipitation. However, these processes are effective and economic only in the case where contamination concentrations are relatively high. Currently sorption process is proved to be one of the effective and attractive processes for the treatment of wastewaters. Also this method will become inexpensive, if the sorbent material used is of inexpensive material and does not require any expensive additional pretreatment step. The major advantages of an adsorption system for water pollution control are less investment in terms of initial cost, simple design and easy operation, less energy intensiveness, non-toxic, and superior removal of organic waste constituents as compared to the conventional biological treatment processes. The adsorption capacity of AC depends mainly on the type of precursor used and the method of preparation.

Zohreshahryari and Ataallah Soltanigoharrizi [68]have studied about the adsorption of methylene blue on the carbon nano tubes. In this study methylene blue was chosen to investigate

the adsorption behaviour of the basic dye from aqueous solution on carbon nano tube. Sorption of methylene blue on carbon nano tube was determined at 287K, 300K, and 310K with 10mg/l as the initial concentration of methylene blue. Sorption equilibrium was attained at 120min. The effects of various process parameters such as dye concentration, carbon nano tube dosage, and temperature on adsorption efficiency were also investigated. It was observed that when the initial dye concentration is increased the percentage of adsorption decreased. This is obvious from the fact that for a constant dosage of adsorbent equilibrium concentration of dye increases but with increasing the initial concentration of dye, then the adsorption percent decreases. Along with increase of sorbent dosage from 20mg/l-400mg/l the percentage of dye adsorbed increases from 20.795%-98.909%. The excellent ability and economic promise of the AC prepared from biomass exhibited high sorption properties. Kannan and sundaram [69] reported that the adsorption capacity of 472.10mg/gm of ACs depends upon the sources of the raw materials used, the history of its preparation and treatment conditions such as pyrolysis temperature and activation time. Many other factors can also affect the adsorption capacity in the same sorption conditions such as surface chemistry (heteroatom content), surface charge and pore structure. A suitable carbon should possess not only a porous texture, but also high surface area. Recently, Guo.etal [70] showed that the adsorption does not always increase with the surface area. Besides the physical structure, adsorption capacity of the given carbon is strongly influenced by the chemical nature of surface.

V k Gupta and suhas [71] reviewed the application of low-cost adsorbents for dye removal and also studies about the different methods of dye removal from industrial waste water. In this study the authors reviewed the steps for industrial waste-water treatment process. Pre-treatment of industrial waste water streams prior to discharge to municipal sewage system or even central industrial sewage system are pre-treated doing equalization-neutralization; then they undergo the primary treatment and waste water is directed towards removal of pollutants with less effort. Suspended oils are removed by either physical or chemical separation techniques and handled as concentrated solids; then they are given a secondary treatment usually involving microorganisms (biological treatment) primarily bacteria which stabilize waste components. The third step is physical treatment or tertiary treatment and the process included in this are adsorption, ion-exchange, and stripping, chemical oxidation and membrane separations. All of these are more expensive than biological treatment but are used for removal of pollutants that are

not easily removed by biological methods. On searching for economical and available starting materials; different low cost adsorbents were used for the removal of dyes [72]. Activated rice-husk was used as a cheap adsorbent for the colour removal from waste water [73]. The maximum adsorption capacity of basic dye methylene blue on to cedar dust and crushed brick was 60mg/l and 40mg/l respectively. [74]. All carbon samples were found to have high or very high methylene blue retaining capacity, as compared with commercial grade carbons. Values are ranging between a minimum of 287 mg/gm for tire char to a maximum of 598 mg/gm for lignite. Calgon F300 commercial product possesses a methylene blue adsorption capacity of 240 mg/gm. [75]. Yaminyasin et.al, [76] studied about the adsorption of methylene blue onto treated AC. In this study they indicated that the treated AC was an alternative candidate for removing organic dye of methylene blue which shows great reduction of colour while reducing the time contact to achieve equilibrium. Phosphoric acids ACs are the best uptake of methylene blue from aqueous solutions (200 mg/gm-400mg/gm) [77].

Shah J et.al, [11] studied about the adsorption of methylene blue on the activated carbon prepared from waste tire char. In this study the activation temperature for the preparation of activated carbon is maintained at 900°C for 2hours with 1000mg/dm^3 as the initial concentration, HCL and H2SO4 are used as activating agents for the preparation of activated carbon. Adsorption capacities of methylene blue on acid treated activated carbon is observed and compared to commercial activated carbon. Amount of methylene blue adsorbed on the prepared activated carbon is found to be 18 (mg/gm) (when HCL is used as activating agent) and 17 (mg/gm) (when H_2SO_4 is used as activating agent). Miguel G.S et.al, [78] studied about the adsorption capacity of methylene blue on activated carbon prepared from waste tire at an activation temperature of 300°C-1000°C, under nitrogen flow with initial concentration at 300 (mg/lit). The amount of methylene blue adsorbed on activated carbon prepared is observed to be 52 (mg/gm). Adsorption capacity of methylene blue on the activated carbon prepared from bamboo based activated carbon increases from 100 (mg/gm)-420 (mg/gm) upon increase in initial concentration from 100 (mg/lit)-500 (mg/lit), prepared at an activation temperature of 700°C using KOH as activating agent [79]. Yang et.al, [86] studied about the preparation of activated carbon from walnut shells at an activation temperature of 450°C by using $ZnCl_2$ as activating agent at an initial concentration of 200 (mg/lit). Amount of methylene blue adsorbed on the prepared activated carbon is found to be 315 (mg/gm). Stavropolous G.G et.al, [7] studied

about the production and characterization of activated carbon prepared from olive-seed waste residue. In this study olive-seed waste residue char was employed as the precursor for the production of activated carbon by using KOH as activating agent. The effects of activation time and activation temperature on the porosity of prepared carbons were also studied. Activation temperature used for the preparation of activated carbon is 800°C and 900°C, at an initial concentration of 500mg/dm^3. Amount of methylene blue adsorbed on the prepared activated carbon is observed as 0.2 (mg/gm) (at 800°C) and 0.22 (mg/gm) (at 900°C) respectively.

List of different types of precursors, preparing conditions and their adsorption capacities for methylene blue are shown in the following table:

Table-2.4 List of Different Types of Precursors, Preparing Conditions and Their Adsorption Capacities in aqueous phase:

S. NO	Precursor	Preparation conditions	Amount adsorbed (Q_e)	Reference
1	Olive seed waste residue	Activation temperature-800°C and 900°C, Activating agent-KOH, C_o-500mg/dm^3	800°C- 0.2 (mg/gm) 900°C- 0.22 (mg/gm)	Stavropoulos G.G etal.,(7)
2	Waste tire char	Activation temperature-900°C and 2hours, Activating agent-HCL and H_2SO_4, C_o-1000mg/dm^3	HCL-18 (mg/gm) H_2SO_4- 17 (mg/gm)	Shah J etal.,(11)
3	Waste tire	Activation temperature-300°C-1000°C, Activating agent- under nitrogen flow, C_o-300 (mg/lit)	52 (mg/gm)	Miguel G.S etal.,(78)
4	Used tires	Activation temperature -550°C, Activating agent-under nitrogen flow, C_o-800ppm	122 (mg/gm)	Helleur R etal.,(33)
5	Bamboo based AC	Activation temperature-700°C and 1hour, Activating agent-KOH, C_o-100(mg/lit)-500(mg/lit)	Increases from 100 (mg/gm)- 420 (mg/gm)	Ahmd A.L etal.,(79)

6	Coconut shells, Coconut fibers	Activation Temperature-600°C, Activating agent-H_2SO_4, C_o-1 (mg/lit)-100 (mg/lit)	16.4 (mg/gm)	Mohan etal., (85)
7	Walnut shells	Activation Temperature-450°C, Activating agent- $ZnCl_2$, C_o-200 (mg/lit)	315 (mg/gm)	Yang etal., (86)
8	Tamarind Wood	Activation Temperature-439°C and 40min, Activating agent-$ZnCl_2$, C_o-10 (mg/lit)-50 (mg/lit)	28.02 (mg/gm)	Acharya etal., (39)
9	Saw Dust	Activation Temperature-650°C and 2hrs, Activating agent-CO_2, 650°C and 2hrs, C_o-100 (mg/lit)-1000 (mg/lit)	24.65 (mg/gm)	Hamadi etal., (87)
10	Hazelnut shell	Activation Temperature-150°C and 24hrs Activating agent-H_2SO_4 C_o-50 (mg/lit)-300 (mg/lit)	170 (mg/gm)	Kobya etal., (88)

2.2.4.2: Effect of process parameters:

2.2.4.2.1: Effect of pH:

The pH factor is a very important factor in the adsorption process especially for dye adsorption. The pH of a medium will control the magnitude of electronic charges which are imparted by the ionized dye molecules. Ould Brahim et al [80] tested the AC prepared from cryogenic grinding of used tires for the adsorption of methylene blue at different pH-values ranges from 2-11. They observed that the methylene blue adsorption increased from 86%-93% as pH varied from 2-11. The increase in the removal of methylene blue with increase in pH is due to a high pH solution, the positive charge at solution interface decreases and the adsorbent surface appears negatively charged [81]. It resulted in higher force of attraction between cationic methylene blue and negatively charged adsorbent surface ultimately leading to higher methylene blue adsorption [82].

2.2.4.2.2: Effect of Contact Time:

Ould Brahmin et al., [80] studied about the adsorption of cationic dye (methylene blue) by AC prepared from cryogenic grinding of used tires. In this study we observe that the sorption % is increased with increasing contact time initially and becomes almost constant after 114 min of contact, it is evident that for the investigated initial concentration of methylene blue, maximum adsorption rate of 93% is achieved almost in 114 min of contact. A further increase in the contact time has a negligible effect on the rate of methylene blue adsorption. Same results were reported by [83].

2.2.4.2.3: Effect of Adsorbent Dose:

Study of the effect of adsorbent dose gives an idea of the effectiveness of the adsorbent and the ability of dye adsorbed with the maximum dosage. In one of the study the dye removal efficiency increased with the adsorbent dosage, this is due to the availability of more binding sites as the dose of bio sorbent increases [80]. However the removal will grow upto a certain limit and then remain constant, the limit in each case is still related to the effect of adsorbate on adsorption. M.S. Kini et al., [84] observed that the methylene blue sorption increases from 40.75%-91.65% at equilibrium as the adsorbent (palm tree male flower) dose increases from 0.05gm-0.30gm.

Chapter-3

Materials and Methods

3.0 Summary:

This chapter describes in detail about various materials, chemical reagents and the methodologies followed to achieve the objectives of the study. The methodology mainly includes characterization of precursor, preparation and characterization of AC and applications of AC in methylene blue adsorption process.

3.1 Materials and Chemicals Used:

Waste tire, Biomass (castor seed mixed with different catalysts) chars and Rice Husk carbon collected from chemical engineering department N.I.T Rourkela, Potassium hydroxide (KOH), Hydrochloric acid (HCL), Methylene Blue, Commercial AC prepared from coconut shell procured from Kalpaka chemicals, Tuticorin, India.

Three catalyst were used namely Bentonite, Molecular sieve, Zeolite. Bentonite used in the process was colloidal native hydrated aluminum silicate, Molecular sieve used in the experiment was of 13X category and is crystalline sodium aluminosilcate. Its specifications are pore size of 10 Å, bulk density of 0.55~0.65, Attrition Abrasion of 0.3~0.5. It is used in desiccation, desulphurization and purification of petroleum gas and natural gas, Zeolite is a microporous aluminosilcate minerals commonly used as commercial adsorbents.

3.2 Methodology:

3.2.1 Characterization of Precursor:

Composition of raw material is an important factor that dictates the selection of precursor for the AC preparation. Various properties of the precursor were characterized by following standard procedures.

3.2.1.1 Proximate Analysis:

The proximate analysis was done by ASTM D3173-75. This analysis is used to determine the moisture content, volatile content, and ash content of the precursor selected.

3.2.1.2 Elemental Analysis:

The elemental analysis was done by using Elemental CHNSO analyzer (MODEL: VARIAEL CUBE Germany), and is used to determine the amount of carbon, hydrogen, nitrogen and sulphur content present in the precursor.

Table-3.1 and Table-3.2 show the proximate and elemental analysis of precursor selected.

Table-3.1: Proximate analysis of precursor selected

	Tyre char	Biomass char (CS)			
		CS	CS (Zeolyte Catalyst used)	CS (Molecular Sieve Catalyst used)	CS (Bentonite Catalyst used)
Moisture Content (weight %)	1.6	7.3	8.8	8.2	4.8
Volatile Content (weight %)	5.28	14.6	17.76	15.03	10.71
Ash Content (weight %)	6.65	7.25	6.93	12.82	1.88
Fixed Carbon (weight %)	86.47	70.85	66.51	63.95	82.61

Table-3.2: Elemental Analysis of Precursor

	Tyre char	Biomass char (CS)			
		CS	CS (Zeolyte Catalyst used)	CS (Molecular Sieve Catalyst used)	CS (Bentonite Catalyst used)
Carbon (Weight %)	79.08	40	36.96	41.01	36.87
Hydrogen (Weight %)	0.52	1.56	1.82	1.50	1.36
Nitrogen (Weight %)	0.46	2.2	1.819	1.95	2
Sulphur (Weight %)	4.61	1	0.27	0.25	1.19

3.2.2 Preparation of AC:

Basically there are two different processes for the preparation of AC from the precursor selected: Physical activation and chemical activation. In the present experiment chemical activation process is followed for the preparation of AC from precursor. Tubular furnace (Figure-3.1) is used for chemical activation of tire and biomass (castor seed mixed with different catalysts) char. 20g of char was initially mixed with 0.1N potassium hydroxide (KOH) solution and left aside for some time, then the mixed Char-KOH slurry was subjected to drying at 110°C for 7-10 hours. The chemically loaded samples were then kept in tubular furnace for activation process in N_2-atmosphere with a flow of 0.5lit/min, at different temperature range from 300°C-700°C, followed by holding the samples at the treatment temperature for an activation time of 30 min before cooling under nitrogen atmosphere. After cooling, the products were washed by stirring with 0.5N HCL solution at 80°C for 30 min (Figure-3.2) followed by filtration (Figure-3.3). The acid washed samples were then leached by mixing with distilled water, leaching of samples was carried out several times until the pH of water-carbon mixture was above 6. The leached products were then dried at110°C for 10-12 hours to get the final product.

Figure- 3.1 *Experimental Setup used for preparation of AC:*

Detailed Explanation :(Specifications)

1. MODEL - VBCC / FUR / 1200ºC (Tubular)/2013/14
2. OPERATING TEMP - 1200ºC (MAX)
3. RATE OF HEATING - 5 Deg C Per Minute(Max)
4. THERMOCOUPLE - K – TYPE
5. Tubular Material - High Alumina [50X60X1000mm]

3.2.3 Characterization of AC:

Various properties of prepared ACs were characterized by following the standard procedures.

3.2.3.1 Proximate analysis:

The moisture content was found by oven-drying test method. A sample of carbon is put into a dry, closed capsule (of known weight) and weighed accurately. The capsule is opened and placed with the lid in a preheated oven (110°C). The sample was dried to constant weight and then was removed from the oven and with the capsule closed, cooled to room temperature. The closed capsule was weighed again accurately. The percentage difference of weight was taken as the moisture content of the sample.

The percentage of volatile matter of the AC samples was determined by the standard method. The sample was taken in crucible with cover (of known weight), and the covered crucible was placed in muffle furnace regulated at 950°C for 7 min. Then the covered crucible was cooled to room temperature in desiccator and the weight was recorded. The percentage weight loss was regarded as the percentage of volatile matter.

To determine the ash content, the sample of AC was taken in the crucible (of known weight) and then placed in the muffle furnace at 550°C and ashing was considered to be completed when constant weight was achieved. The crucible was cooled to room temperature in a desiccator and the percentage weight of the sample remained was considered as ash content.

Fixed carbon is a calculated value and it is the resultant of summation of percentage moisture, ash, and volatile matter subtracted from 100.

Fixed carbon (%) = 100 – (moisture, % + ash, % + volatile matter, %)→ (A)

3.2.3.2 Elemental analysis:

The ultimate analysis or elemental analysis was carried out by using CHNS analyzer. The percentage of oxygen was calculated by the difference as follows.

Oxygen (%) = 100 – (C, % + H, % + N, % + S, %)→ (B)

3.2.3.3 Yield%:

The yield of AC was calculated on a chemical-free basis and can be regarded as an indicator of the process efficiency for the chemical activation process. The yield of AC was calculated as the percentage weight of the resultant AC divided by weight of waste tire char (raw char).

$$yield\% = \frac{weightofactivatedcarbonaftercarbonization}{weightofrawmaterial} \times 100 \rightarrow (C)$$

3**.2.3.4 Surface Area of AC Prepared**:

Nitrogen (N2) gas adsorption-desorption isotherms on prepared ACs at liquid nitrogen temperature (77K) were carried out using an automatic adsorption unit, Autosorb–1 (Quanta chrome). The samples were degassed at 200°C for 5 h prior to analysis so as to remove any adsorbed moisture or other impurities bound to the surface of the sample. Surface area values were calculated from the experimental adsorption isotherm over a relative pressure range of 0.01 to 0.3 using the standard BET (Brunauer, Emmett and Teller) method. The BET equation is given as,

$$\frac{p}{v(p^o - p)} = \frac{1}{v_m C} + \frac{C-1}{v_m C}\left(\frac{p}{p^o}\right) \rightarrow (D)$$

Where, *V* is the volume adsorbed at STP (cm_3g^{-1}), v_m is the volume of monolayer capacity atSTP (cm3g-1), and the term *C*, the BET constant, are related to the energy of adsorption in the first adsorbed layer and its value is an indication of the magnitude of the adsorbent-adsorbate interactions.

3.2.3.5 Fourier Transform Infrared Spectroscopy (FTIR):

The prepared AC was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra were collected in the range of 400-4000cm^{-1}. The FTIR imaging was carried out using Perkin Elmer RX.

3.2.3.6 Scanning Electron Microscope (SEM):

SEM is used to determine the morphology of the material under view. Images are produced of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. The surface of the char obtained was viewed under a Scanning Electron Microscope (Model: JEOL-JSM-6480LV SEM) at different magnification values.

3.2.4 Adsorption Experiments:

Methylene blue which is a relatively large molecule was employed as adsorbate in liquid phase adsorption. 100ppm of stock solution was prepared initially. In this process effect of various process parameters like contact time, pH, and adsorbent dose of AC prepared were investigated. UV-visible spectrophotometer was used (at a specific wave length range of 660nm) for the determination of absorbance value.

Effect of contact time:

30ml of stock solution was taken in 5-conical flasks each initially. AC of 0.2g was added in all the flasks and then kept in an incubator shaker for shaking process at different intervals of time from 5-25 min. After shaking, the samples were then filtered and the liquid samples remained in

flask after filtration was taken for UV-analysis (absorbance determination). Finally the amount of dye adsorbed Q_e(mg/gm) and the percentage of adsorption was calculated.

Effect of pH:

30ml of stock solution was taken in conical flasks initially, and pH of the samples was adjusted from 2-10 using pH meter. AC of 1gram was added in all the flasks and then kept in an incubator shaker for shaking process for a time interval of 5hours. After shaking, the samples were filtered. This was followed by absorbance determination (UV- analysis) using UV-visible spectrophotometer. Finally the amount of dye adsorbed Q_e(mg/gm) and the percentage of adsorption was calculated.

Effect of Adsorbent Dose:

Initially 30ml of stock solution was taken in conical flasks, and the prepared ACs of different weights from 0.2gm-1gm were added into flasks followed by the shaking process for a time interval of 2hours. After shaking, the samples were filtered and then taken for absorbance determination (UV-analysis). Finally the amount of dye adsorbed Q_e(mg/gm) and the percentage of adsorption was calculated.

The adsorption percentage and adsorption capacity (Q_e (mg/gm)) of prepared AC for methylene blue were calculated based on the following equations:

$$Adsorption\ \% = \frac{Co-Ce}{Co} \times 100 \quad \rightarrow (E)$$

Where $Co \rightarrow initial\ concentration\left(\frac{mg}{lit}\right)$

$Ce \rightarrow equilibrium\ concentration\left(\frac{mg}{lit}\right)$

$$Adsorption\ Capacity(Qe) = \frac{(Co - Ce) \times v}{m} \quad \rightarrow (F)$$

Where $Co \rightarrow initial\ concentration\left(\frac{mg}{lit}\right)$

$Ce \rightarrow equilibrium\ concentration\left(\frac{mg}{lit}\right)$

$v \rightarrow volume\ of\ sample\ taken(liter)$

$m \rightarrow mass\ of\ adsorbate\ used(gram)$

Figure-*3.2*: Process of heating AC with 0.5N HCL solution:

Figure-3.3: Process of filtration followed after heating:

Figures for Adsorption Experiments:

Figure-3.4*:* Samples for UV-analysis before shaking in shaker.

Figure-3.5 Samples for UV-analysis after shaking in shaker.

3.2.4.1 Adsorption Equilibrium Study:

Adsorption equilibrium isotherms on the prepared ACs were determined. For these experiments flasks were incubated at constant temperature (30°C) and agitation speed (120rpm), for 5hours of contact time to attain equilibrium. The isotherm models used in present study are Langmuir isotherm and Freundlich isotherm.

Langmuir Isotherm:

The Langmuir isotherm model is applicable to homogenous sorption where the sorption of each sorbate molecule on to the surface has equal sorption activation energy and is represented as follows.

$$qe = \frac{QoKCe}{1+KCe} \rightarrow \quad (G)$$

The linear form of Langmuir isotherm equation is given as

$$\frac{1}{qe} = \frac{1}{Qo} + \left[\frac{1}{KQo}\frac{1}{Ce}\right] \rightarrow \quad (H)$$

Where $qe \rightarrow \ solid\ phase\ sorbate\ concentration\ at\ equilibrium$

$$Ce \rightarrow \ liquid\ phase\ sorbent\ concentration\ at\ equilibrium$$

$$Qo \rightarrow monolayer\ saturation\ capacity = \frac{K}{a}$$

$$K, a \rightarrow Langmuir\ isotherm\ constants$$

The adsorption data were analyzed according to linear form of equation (Equation (H)). The essential characteristics of Langmuir isotherm can be explained in terms of dimensionless constant, separation factor (R) which is represented as

$$R \ = \frac{1}{1+aCi} \rightarrow \quad (I)$$

Where $Ci \rightarrow initial\ concentration$

The value of R, a positive number ($0 < R < 1$), signifies the feasibility of the adsorption process for all developed ACs.

Freundlich Isotherm:

The most important multilayer adsorption isotherm for heterogeneous surfaces is the Freundlich isotherm which is characterized by the heterogeneity factor 1/n and is represented by the equation

$$q_e = K_f C e^{1/n} \qquad \rightarrow (J)$$

Where $qe \rightarrow solid\ phase\ sorbate\ concentration\ at\ equilibrium$

$Ce \rightarrow liquid\ phase\ sorbent\ concentration\ at\ equilibrium$

$K_f \rightarrow Freundlich\ constant$ and

$1/n \rightarrow heterogeneity\ factor$

The linear form of Freundlich isotherm equation is given as

$$\log (q_e) = \log (K_f) + 1/n\ (\log (C_e) \quad \rightarrow (K)$$

Where the intercept log (K_f) is the measure of adsorption capacity, and the slope 1/n is the adsorption intensity. The values of K_f and n were calculated from the intercept and slope of the plot of log (q_e) versus log (C_e).

Chapter 4

Result and Discussions

4.0 Summary:

This chapter describes in detail the result and discussions of experimental work carried on characterization and applications of AC from tire and biomass (CS) with char.

4.1 Characterization of AC:

4.1.1 Proximate Analysis:

Table-4.1: Proximate analysis of AC prepared from tire and biomass (CS)

	Tyre char	Biomass char (CS)				Commercial Carbon
		CS	CS (Zeolyte Catalyst used)	CS (Molecular Sieve Catalyst used)	CS (Bentonite Catalyst used)	
Moisture Content (weight %)	2	7.2	10	4	6	6.11
Volatile Content (weight %)	7.55	18.4	18.57	18.54	17.44	28.73
Ash Content (weight %)	11.69	10.33	10.72	14.83	4.98	0.58
Fixed Carbon (weight %)	78.76	64.1	60.71	71.58	62.63	61.04

4.1.2 Elemental Analysis:

Table-4.2: Elemental analysis of AC prepared from tire and biomass (CS mixed with different catalysts)

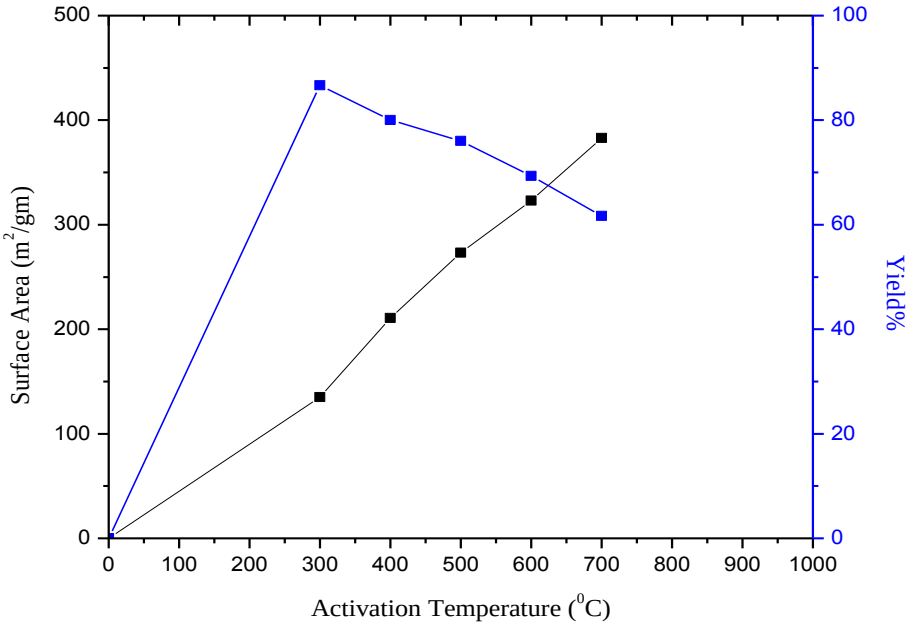
	Tyre char	Biomass char (CS)				
		CS	CS (Zeolyte Catalyst used)	CS (Molecular Sieve Catalyst used)	CS (Bentonite Catalyst used)	Commercial carbon
Carbon (Weight %)	66.23	48	48.31	43.87	52.94	71.24
Hydrogen (Weight %)	3.14	1.5	1.22	1.06	1.74	1.10
Nitrogen (Weight %)	1.74	1.44	1.33	1.06	1.55	2.20
Sulphur (Weight %)	2.78	0.87	0.85	0.81	0.73	0.36
Oxygen (weight %)	26.11	48.19	48.29	53.2	43.04	25.1

Table-4.1 and Table-4.2 shows the proximate and elemental analysis of the prepared AC and commercial carbon. Proximate analysis (was done by using ASTM D3173-75) highlights that the prepared AC and commercial carbon are having less moisture content and the high carbon content. Elemental analysis was done by using elemental CHNS analyzer highlights that the prepared AC and commercial carbon has negligible sulphur content and more carbon and oxygen contents.

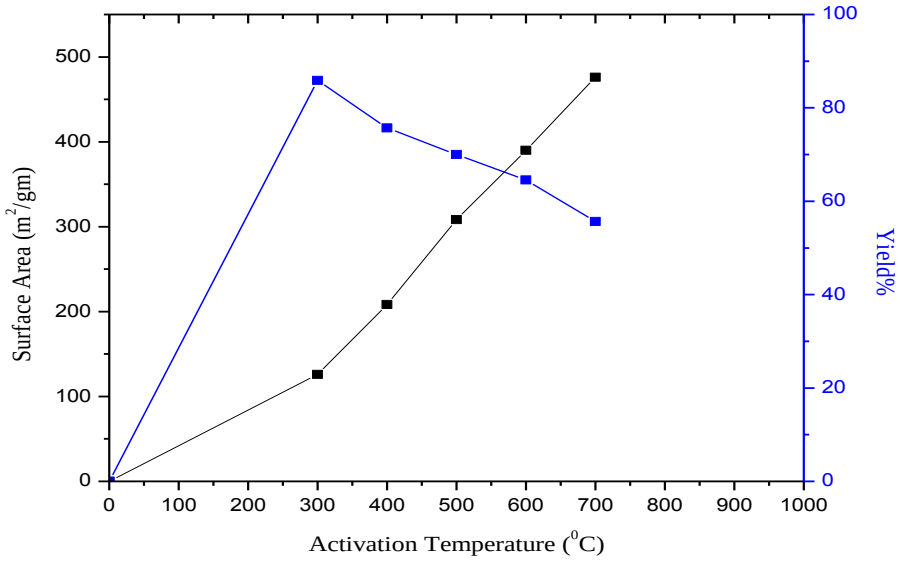
4.1.3 Effect of activation temperature on yield% and surface area of prepared AC:

In the preparation of AC the effect of activation temperature on yield% and surface area of the prepared carbon on activation temperature has been investigated. The following plots

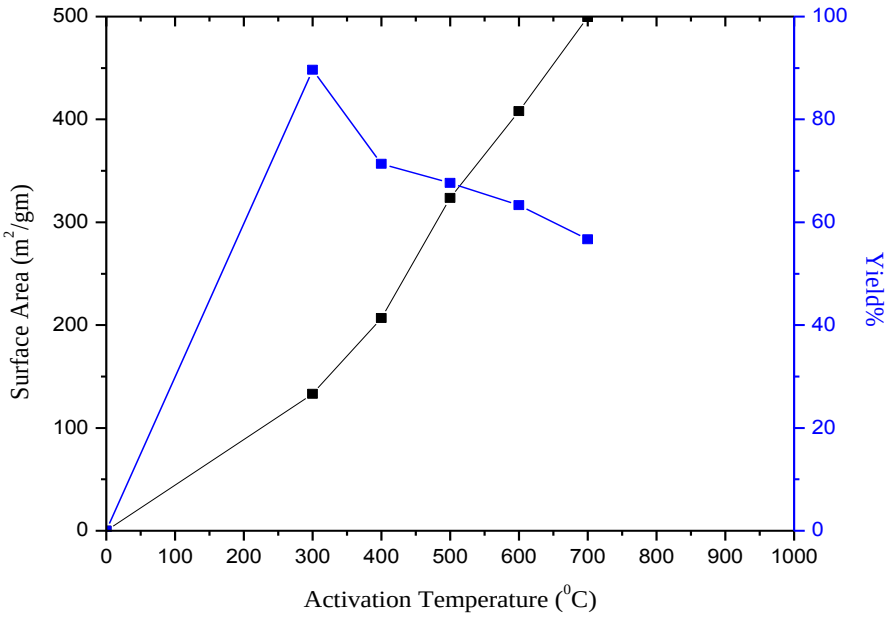
(Figure-4.1) Effect of activation temperature on yield% and surface area of tyre derived AC:



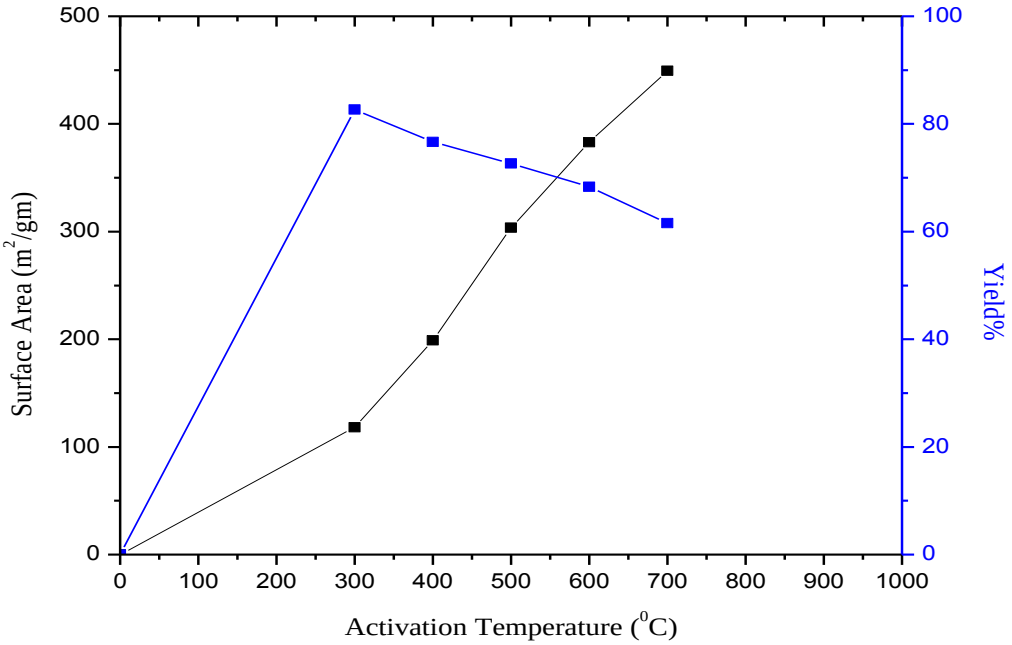
(Figure-4.2) Effect of activation temperature on yield% and surface area of biomass (CS) AC:



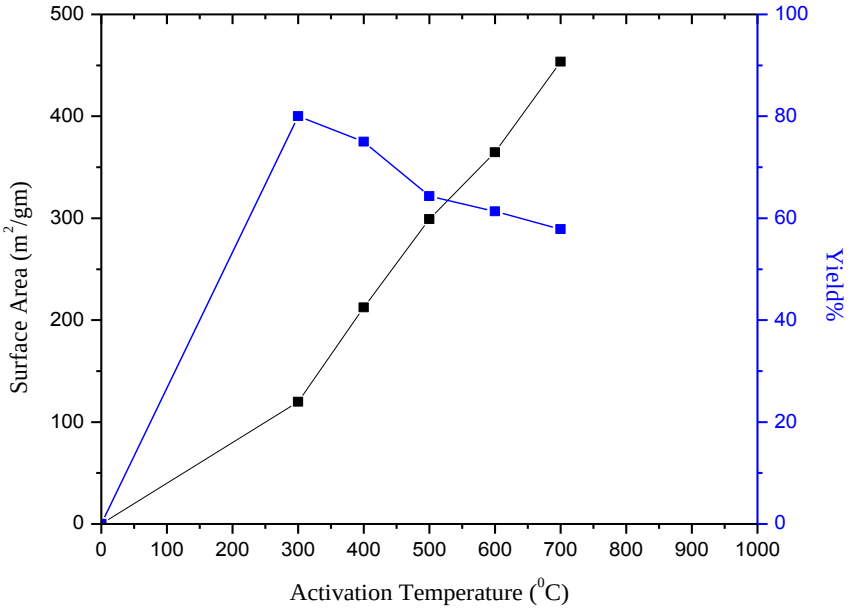
(Figure-4.3) Effect of activation temperature on yield% and surface area of biomass (CS with Zeolite Catalyst) AC:



(Figure-4.4) Effect of activation temperature on yield% and surface area of biomass (CS with Bentonite Catalyst) AC:



(Figure-4.5) Effect of activation temperature on yield% and surface area of biomass (CS with Molecular Sieve Catalyst) AC:



From (Figure-4.1) - (Figure-4.5) we observe that by increasing the activation temperature from 300°C-700°C the yield% of AC decreases from 86.67%-61.65% for tyre derived AC; from 85.89%-55.68% for biomass (CS) AC; from 89.67%-56.65% for biomass (CS mixed with Zeolyte as catalyst) AC; from 82.67%-61.54% for biomass (CS mixed with bentonite as catalyst) AC; from 80%-57.85% for biomass (CS mixed with molecular sieve as catalyst) AC and the surface area increases to a maximum from 135-382.9 m^2/gm for tyre derived AC; from 126-475.96 m^2/gm for biomass (CS) AC; from 133-499.33 m^2/gm for biomass (CS mixed with Zeolyte as catalyst) AC; from 118.22-449.22 m^2/gm for biomass (CS mixed with bentonite as catalyst) AC; from 120-453.45 m^2/gm for biomass (CS mixed with molecular sieve as catalyst) AC. From the literature we can say that more the surface area leads to a good AC.

4.1.4 Fourier Transform Infrared Spectroscopy (FTIR) analysis of prepared AC:

Fourier Transform Infrared (FTIR) Spectroscopy is one of the important techniques which base its functionality on the principle that almost all molecules absorb infrared light. The FTIR spectrum of the prepared AC for both tire and biomass (CS with different catalysts) char is shown in the following plots.

(Figure-4.6)Fourier Transform Infrared (FTIR) Spectra plots of tyre derived AC:

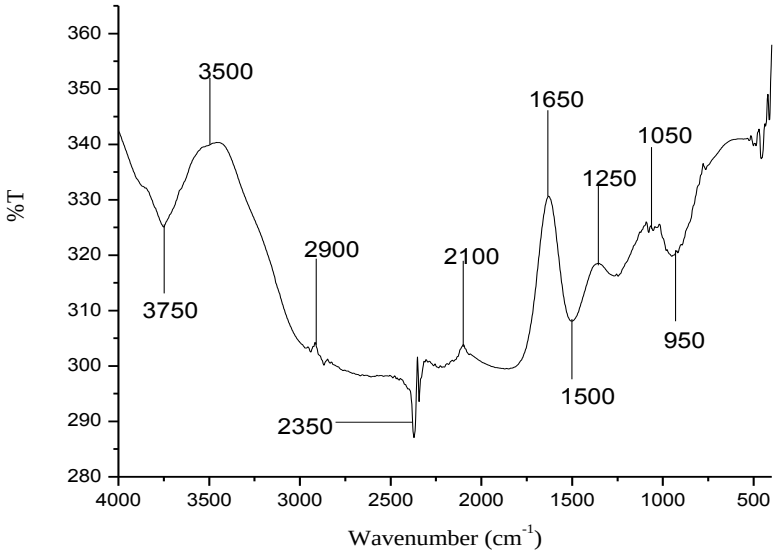


Table-4.3: FTIR functional groups of tire derived AC:

Wavelength Range (Cm^{-1})	Functional Group	Class of Compounds
3750	N-H Stretch	Amides
3500	N-H Stretch	Amides
2900	H-C-H Asymmetric and Symmetric Stretch	Alkanes
2350	C≡N Stretch	Nitriles
2100	C≡C Stretch	Alkynes
1650	C-C=C Symmetric Stretch	Alkenes
1500	H-C-H Bend	Alkanes
1250	C-N Stretch	Aliphatic Amines
1050	C-O Stretch	Ethers
950	O-H Bend	Carboxylic acids

From Figure-(4.6) we observe the FTIR analysis of AC prepared from tire char. We observe a broad peak at a wave length of 3500 cm^{-1} which is due to the presence of amides groups (N-H Stretch) on the surface. The sharp peaks are observed at a wavelength of 2950cm^{-1} and 1650cm^{-1} which is due to the presence of alkanes (H-C-H asymmetric and symmetric stretch) and alkenes (C-C=C symmetric stretch) groups respectively. Presence of nitriles(C≡N stretch), alkynes (C≡C stretch), and carboxylic acid (C=O stretch) is observed at wavelengths 2350cm^{-1}, 2100cm^{-1}, 1800cm^{-1} respectively. Alkanes (H-C-H bend), is observed at the wave length of 1500cm^{-1}, and carboxylic acids (O-H bend) is observed at 950cm^{-1}.

(Figure-4.7)Fourier Transform Infrared (FTIR) Spectra plots of biomass (CS) AC:

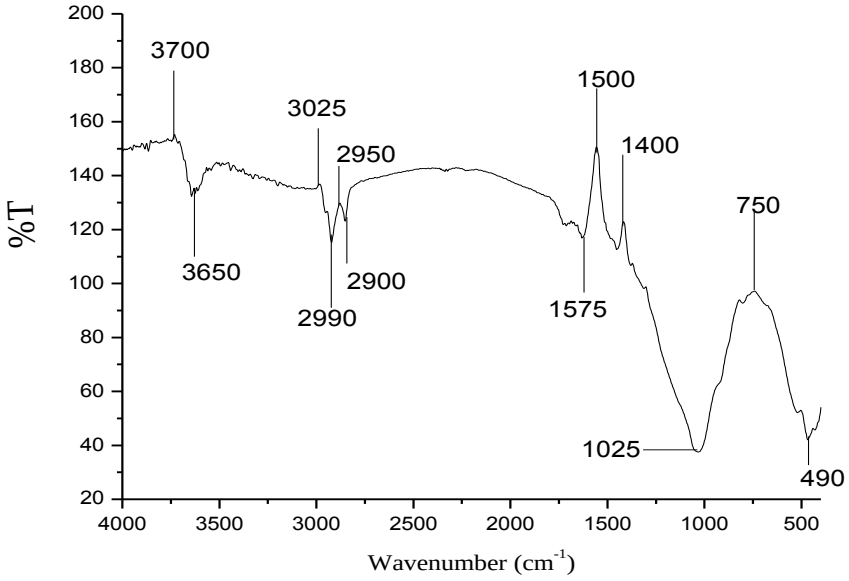


Table-4.4: FTIR functional groups of AC derived from biomass (CS) char:

Wavelength Range (Cm^{-1})	Functional Group	Class of Compounds
3700	N-H Stretch	Amide
3650	N-H Stretch	Amide
3025	C-H Stretch	Alkenyl
2990	O-H Stretch	Carboxylic Acid
2950	O-H Stretch	Carboxylic Acid

2900	O-H Stretch	Carboxylic Acid
1575	C-C=C Symmetric Stretch	Aromatic Rings
1500	H-C-H Bend	Alkanes
1400	N=O Bend	Nitro Groups
1025	C-O Stretch	Ethers
750	C-Cl Stretch	Alkyl Halides
490	C-Br Stretch	Alkyl Halides

From Figure- (4.7) we observe the FTIR analysis of AC prepared from biomass (CS) char. We observe a broad peak at a wave length of 3700 cm^{-1} and 3650cm^{-1} which is due to the presence of amides a group (N-H Stretch) on the surface. The sharp peaks are observed at a wavelength of 2990cm^{-1} and 1500cm^{-1} which is due to the presence of carboxylic acid (O-H stretch) and alkanes (H-C-H Bend) groups respectively. Presence of nitro groups (N=O Bend), ethers (C-O stretch), and alkyl halides (C-Cl stretch) is observed at wavelengths 1400cm^{-1}, 1025cm^{-1}, 750cm^{-1} respectively.

(Figure-4.8)Fourier Transform Infrared (FTIR) Spectra plots of biomass (CS with Zeolite Catalyst) AC:

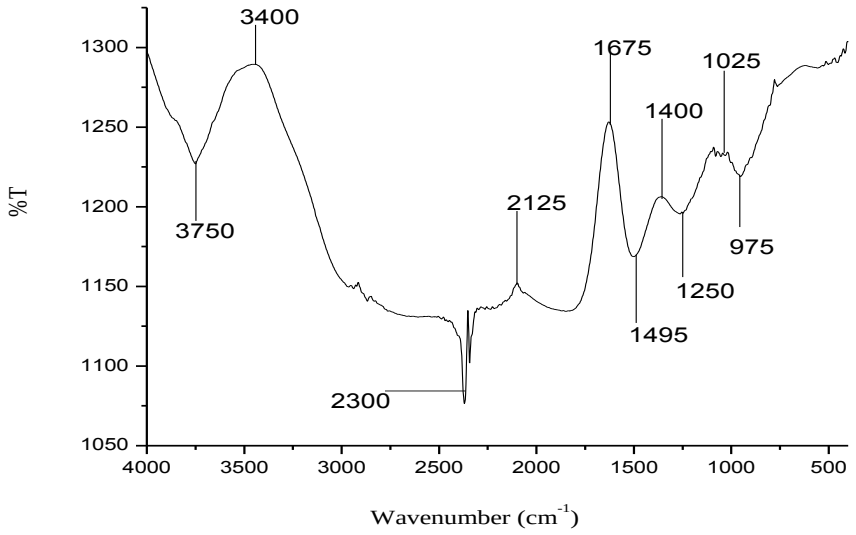


Table-4.5: FTIR functional groups of AC derived from biomass (CS with Zeolite Catalyst) char:

Wavelength Range (Cm^{-1})	Functional Group	Class of Compounds
3750	N-H Stretch	Amide
3400	Hydrogen-bonded O-H Stretch	Phenols and Alcohols
2300	C≡N Stretch	Nitriles
2125	C≡C Stretch	Alkynes
1675	C-C=C Symmetric Stretch	Alkenes
1495	C-C=C Asymmetric Stretch	Aromatic rings
1400	N=O Stretch	Nitro Groups
1250	C-O Stretch	Ethers
1025	C-O Stretch	Ethers
975	=C-H Bend	Alkenes

From Figure-(4.8) we observe the FTIR analysis of AC prepared from biomass (CS mixed with Zeolyte catalyst) char. We observe a broad peak at a wave length of 3400 cm^{-1} which is due to the presence of phenols and alcohols (Hydrogen-bonded O-H Stretch) on the surface. The sharp peaks are observed at a wavelength of 3750 cm^{-1}, 2300cm^{-1}, 2125$cm^{-1}$and 1675 cm^{-1} which is due to the presence of amides (N-H Stretch), nitriles (C≡N Stretch), alkynes (C≡C Stretch), and alkenes (C-C=C Symmetric Stretch) groups respectively. The presence of aromatic rings (C-C=C Asymmetric Stretch), nitro groups (N=O Stretch), and Ethers (C-O Stretch) is observed at wavelengths 1495cm^{-1}, 1400cm^{-1}, 1250cm^{-1} and 1025cm^{-1} respectively. Alkenes (=C-H bend), is observed at the wave length of 975 cm^{-1}.

(Figure-4.9)Fourier Transform Infrared (FTIR) Spectra plots of biomass (CS with Bentonite Catalyst) AC:

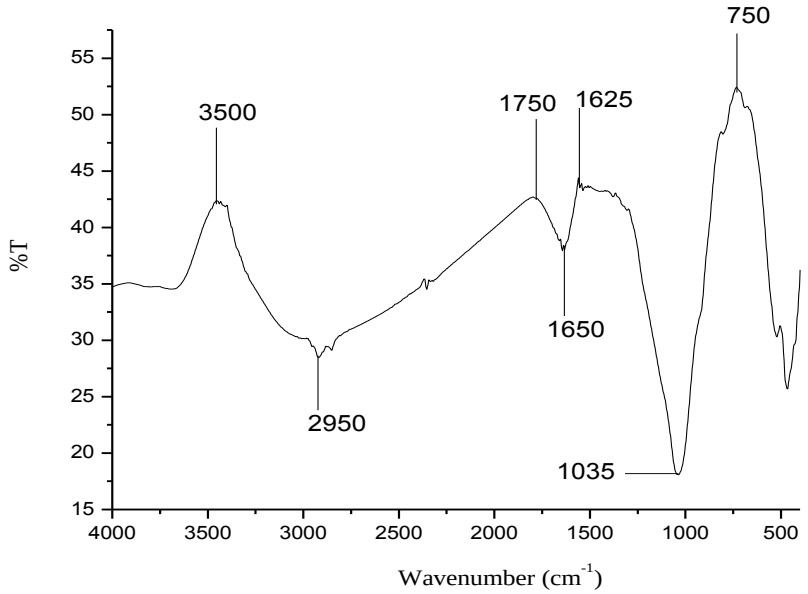


Table-4.6: FTIR functional groups of AC derived from biomass (CS mixed with bentonite as catalyst) char:

Wavelength Range (Cm^{-1})	Functional Group	Class of Compounds
3500	Hydrogen-bonded O-H Stretch	Phenols and Alcohols
2950	H-C-H Asymmetric and Symmetric Stretch	Alkanes
1750	C=O Stretch	Ketones
1650	C-C=C Symmetric Stretch	Alkenes
1625	C-C=C Symmetric Stretch	Alkenes
1035	C-O Stretch	Ethers
750	C-H Bending	Aromatics

From the above plot (Figure-4.9) we observe the FTIR analysis of AC prepared from biomass (CS mixed with Bentonite catalyst). In the above figure a broad peak is observed at a wave length of 3500cm^{-1} which is due to the presence of phenols and alcohols groups (Hydrogen-bonded O-H Stretch). Sharp peaks are observed at wavelengths 1650 cm^{-1}, 1035 cm^{-1}and 750 cm^{-1} which is due to presence of alkenes (C-C=C Symmetric Stretch), ethers (C-O Stretch) and aromatics (C-H bending) respectively. Ketones (C=O Stretch) groups are also observed at wavelength 1750 cm^{-1}.

(Figure-4.10)Fourier Transform Infrared (FTIR) Spectra plots of biomass (CS Molecular Sieve Catalyst) AC:

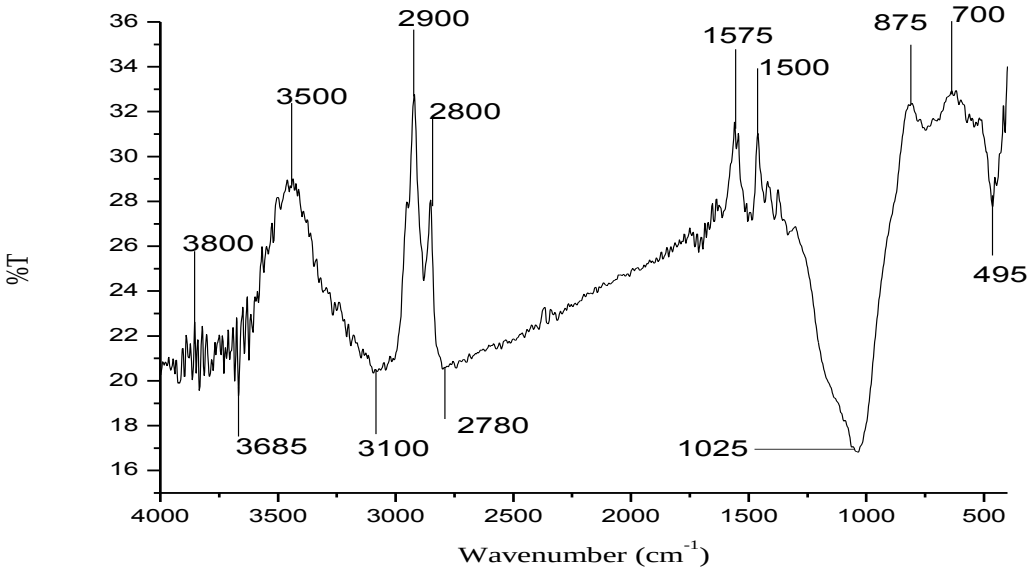


Table-4.7: FTIR functional groups of AC derived from biomass (CS mixed with molecular sieve as catalyst) char

Wavelength Range (Cm^{-1})	Functional Group	Class of Compounds
3800	N-H Stretch	Amide
3685	Hydrogen-bonded O-H Stretch	Phenols and Alcohols
3500	Hydrogen-bonded O-H Stretch	Phenols and Alcohols
3100	Hydrogen-bonded O-H Stretch	Phenols and Alcohols

2900	H-C-H Asymmetric and Symmetric Stretch	Alkanes
2800	H-C-H Asymmetric and Symmetric Stretch	Alkanes
2780	Hydrogen-bonded O-H Stretch	Carboxylic Acids
1575	N-H Bend	Amines-Primary
1500	N=O Stretch	Nitro Groups
1025	C-O Stretch	Ethers
875	C-H Bending	Aromatics
700	C-H Bending	Aromatics
495	C-Br Stretch	Alkyl Halides

From the above plot (Figure-4.10) we observe the FTIR analysis of AC prepared from biomass (CS mixed with Molecular Sieve catalyst). In the above figure a broad peak is observed at a wave length of 3500cm^{-1} which is due to the presence of phenols and alcohols groups (Hydrogen-bonded O-H Stretch). Sharp peaks are observed at wavelengths 2900 cm^{-1}, 2800 cm^{-1}and 1500 cm^{-1} due to presence of alkanes (H-C-H Asymmetric and Symmetric Stretch), and nitro groups (N=O Stretch) respectively. Ethers (C-O Stretch), aromatics (C-H Bending), and alkyl halides (C-Br Stretch) are observed at wavelength 1025cm^{-1}, 875cm^{-1}, 700cm^{-1}, and 495cm^{-1} respectively.

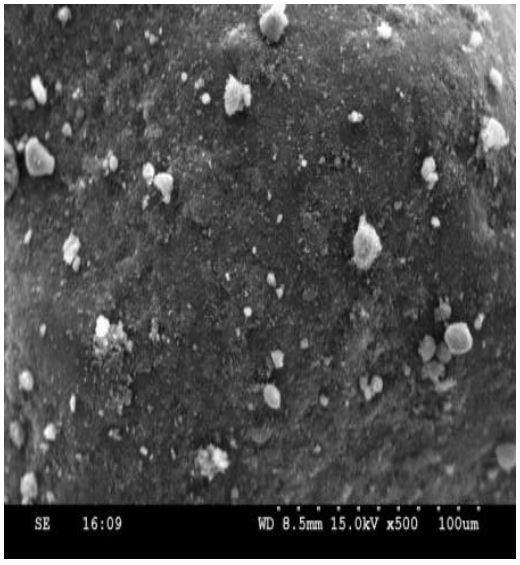
4.1.5: Scanning Electron Microscope (SEM) analysis:

The images of the AC surface obtained from scanning electron microscope (SEM) at different magnification levels. Scanning Electron Microscope (SEM) analysis revealed the surface structure of the samples. SEM images of chemically activated carbons by KOH were presented in figure-4.11. In all the cases the well developed porous surface was observed at higher magnification. The pores observed from SEM images are having diameter in micrometer range. These pores are considered as channels to the microporous network. From the figures it was observed that all the adsorbents have rough texture with heterogeneous surface and variety of randomly distributed pore size. On comparison of all the figures we can say that high porous

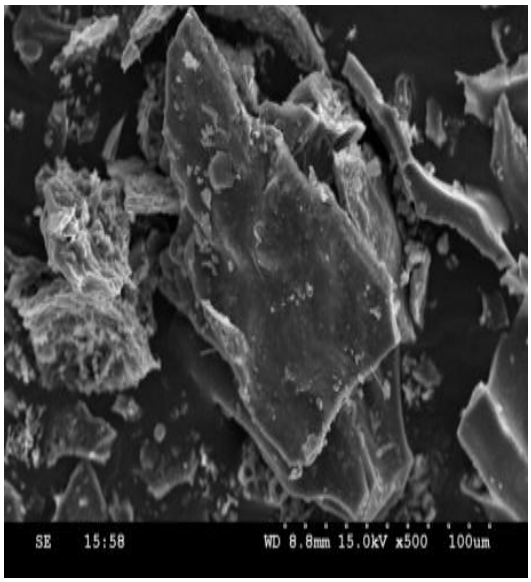
surface can be observed for the sample prepared from biomass (CS) AC upon increase in the magnification level.

Figure-4.11: SEM images of AC prepared:

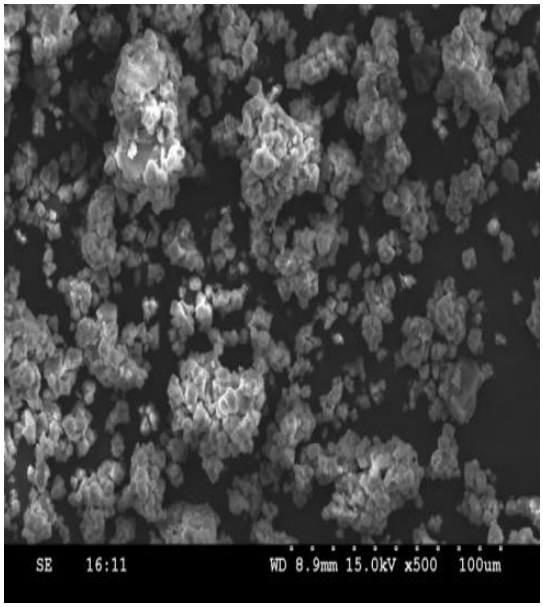
(Figure-4.11$_a$) Tyre derived AC:



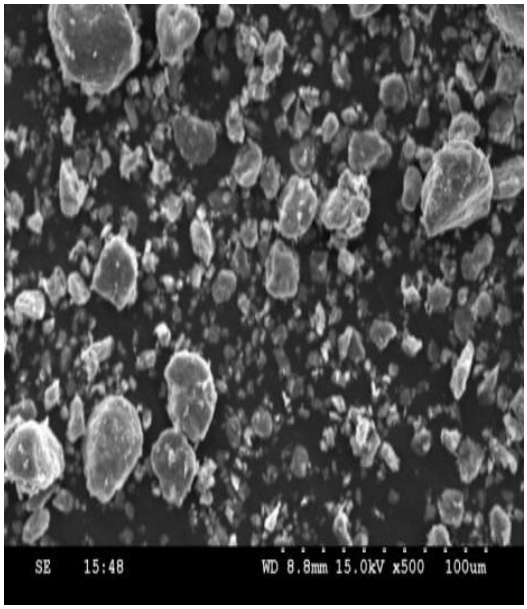
(Figure-4.11$_b$) Biomass (CS) AC:



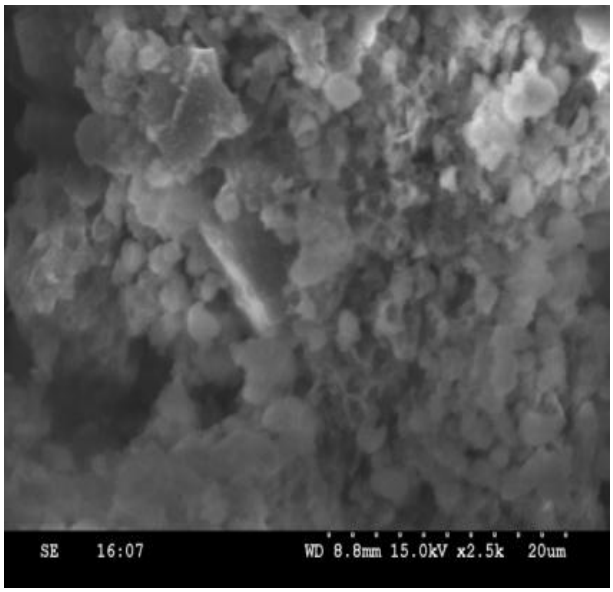
(Figure-4.11$_c$) Biomass (CS with Zeolite Catalyst AC:



(Figure-4.11$_d$) Biomass (CS with Bentonite Catalyst)AC:



(Figure-4.11$_e$) Biomass (CS with Molecular Sieve Catalyst) AC:



4.1.6 Adsorption of Methylene Blue on AC:

Application of AC in methylene blue adsorption is significantly influenced by its method of preparation. Chemical activation method is used for preparation of AC from both tire and biomass (castors seed mixed with different catalysts) chars. KOH is used as chemical activating agent for the preparation of AC. The influence of various process parameters such as effect of contact time, pH, and adsorbent dose is investigated.

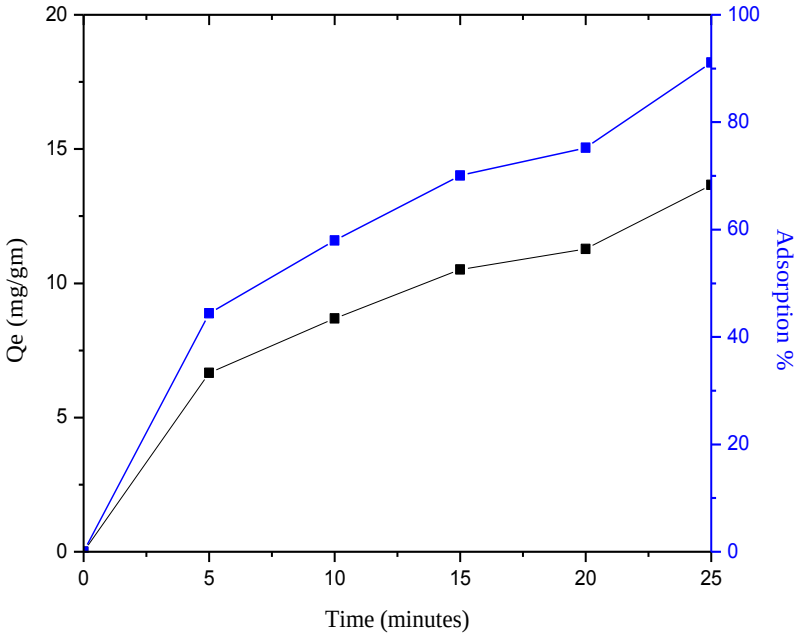
4.1.6.1 Effect of Process Parameters:

4.1.6.1.1 Effect of Contact Time:

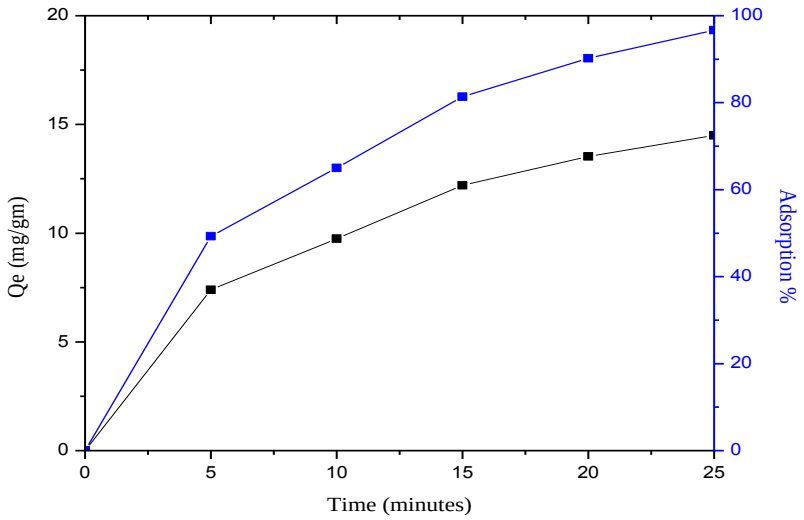
From *Figure-4.12-Figure-4.16*we observed that for the investigated initial concentration of methylene blue the amount of dye adsorbed (Qe (mg/gm)) and adsorption % increases with increasing in contact time and reaches a maximum upto 13.66 (mg/gm) and 91.081% for tyre derived AC (Figure 4.12); 14.60(mg/gm) and 97.335% for biomass (CS) AC (Figure 4.13); 14.50 (mg/gm) and 96.701% for biomass (CS with Zeolyte catalyst) AC (Figure 4.14); 14.571 (mg/gm) and 97.14% for biomass (CS mixed with Bentonite as catalyst) AC (Figure 4.15); 14.531 (mg/gm) and 96.874% for biomass (CS mixed with Molecular Sieve as

catalyst) AC(Figure 4.16), in 25min of contact time respectively. A further increase in contact time has a negligible effect on the rate of methylene blue adsorption. The rate of methylene blue removal is higher due to presence of larger surface area of carbon used for adsorption.

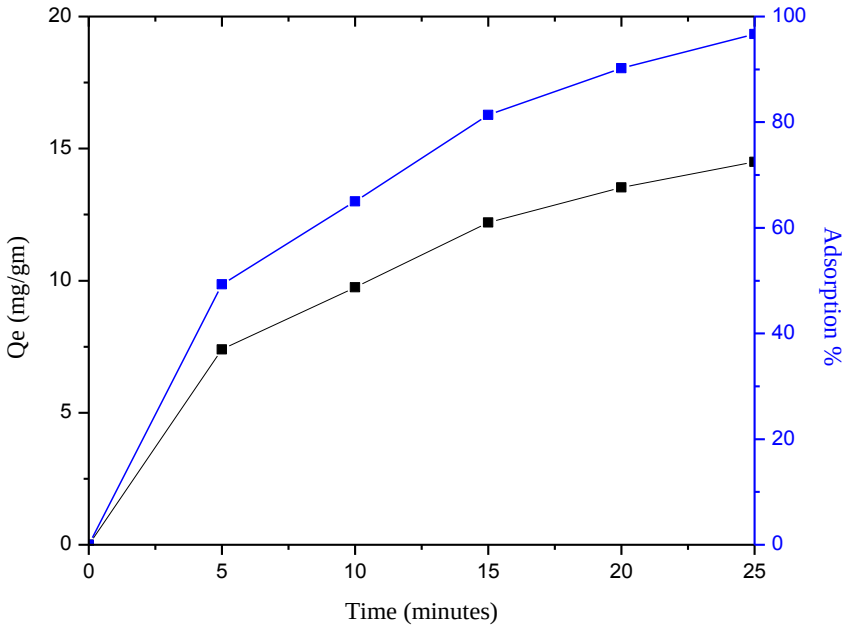
(Figure-4.12)Effect of contact time on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of tyre derived AC:



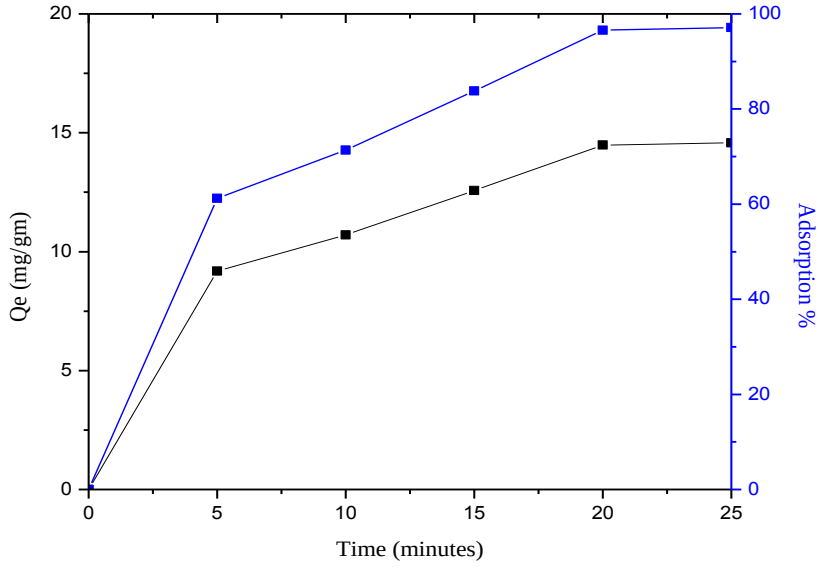
(Figure-4.13) Effect of contact time on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of biomass (CS) AC:



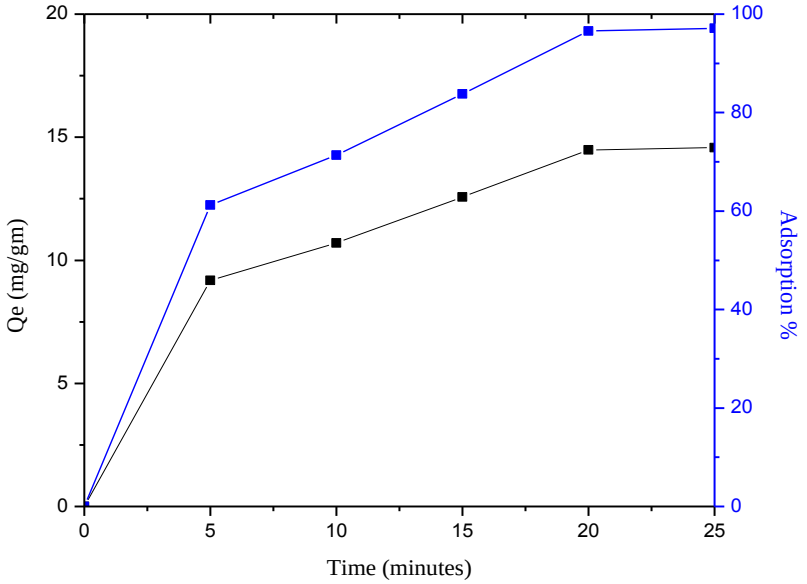
(Figure-4.14) Effect of contact time on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of biomass (CS with Zeolite Catalyst) AC:



(Figure-4.15) Effect of contact time on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of biomass (CS with Bentonite Catalyst) AC:



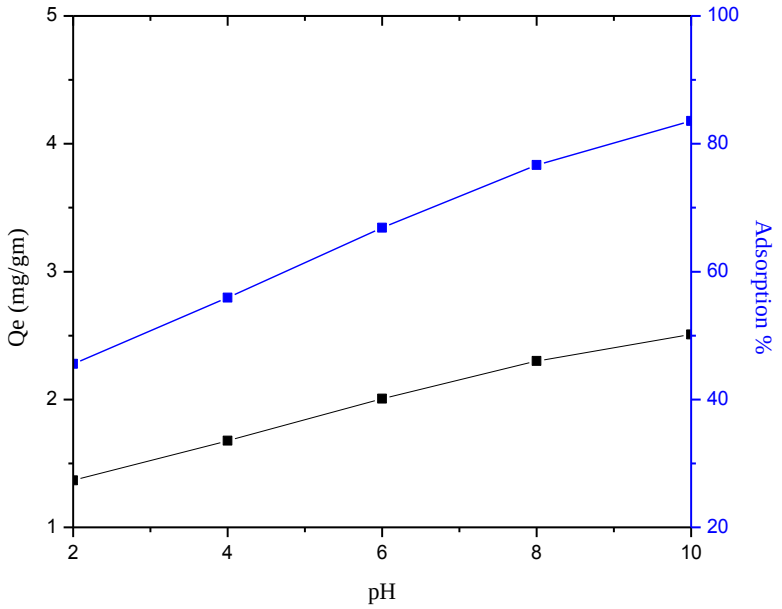
(Figure-4.16) Effect of contact time on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of biomass (CS with Molecular Sieve Catalyst) AC:



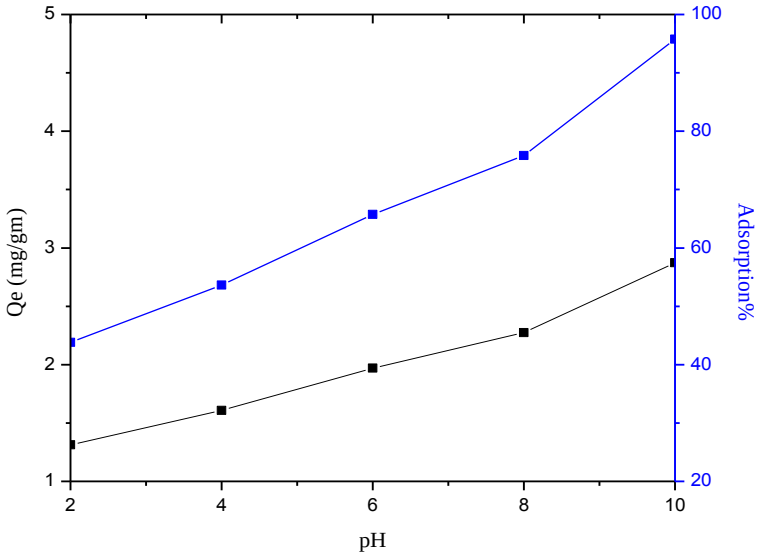
4.1.6.1.2 Effect of pH:

The pH factor is very important in adsorption process especially for methylene blue adsorption. The pH of a medium will control the magnitude of electrostatic charges which are impacted by the ionized methylene blue molecules. The effect of pH on methylene blue removal by AC prepared was investigated over pH range from 2-10. From *Figure-4.17-Figure-4.21* we observe that the amount of dye adsorbed (Qe (mg/gm)) and adsorption% of AC prepared is increased upto a maximum of 2.5077 (mg/gm) and 83.59% for tyre derived AC (*Figure- (4.17)*); 2.872 (mg/gm) and 95.75% for biomass (CS) AC (*Figure- (4.18)*); 2.857 (mg/gm) and 95.26% for biomass (CS with Zeolyte catalyst) AC (*Figure- (4.19)*); 2.6832 (mg/gm) and 89.44% for biomass (CS with Bentonite catalyst) AC (*Figure- (4.20)*); 2.818 (mg/gm) and 93.963% for biomass (CS with molecular sieve catalyst) AC (*Figure- (4.21)*)respectively. At high pH solution, the positive charge at solution interface decreases and the adsorbent surface appears negatively charged resulting in high force of attraction between cationic methylene blue and negatively charged surface ultimately leading to higher methylene blue adsorption.

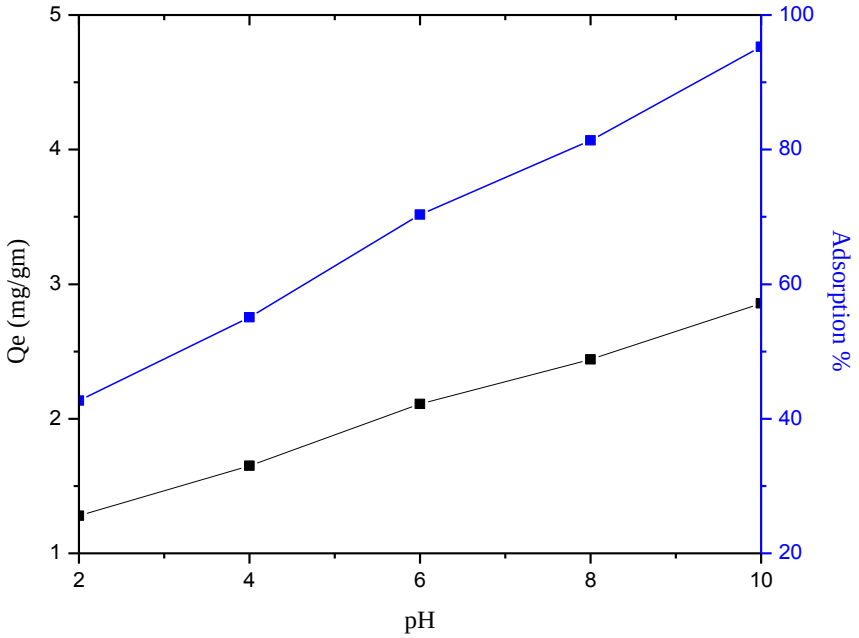
(Figure-4.17) Effect of pH on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of tyre derived AC:



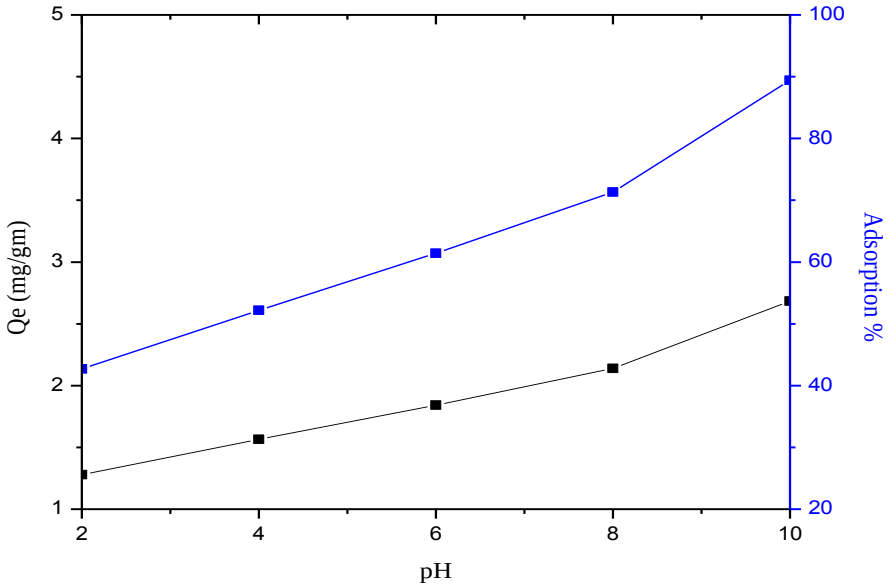
(Figure-4.18) Effect of pH on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of biomass (CS) AC:



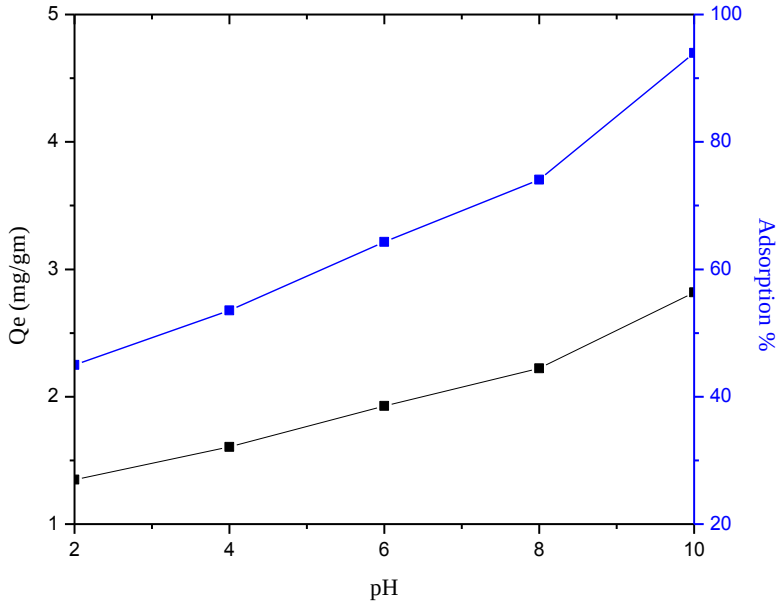
(Figure-4.19) Effect of pH on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of biomass (CS with Zeolite Catalyst) AC:



(Figure-4.20) Effect of pH on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of biomass (CS with Bentonite Catalyst) AC:



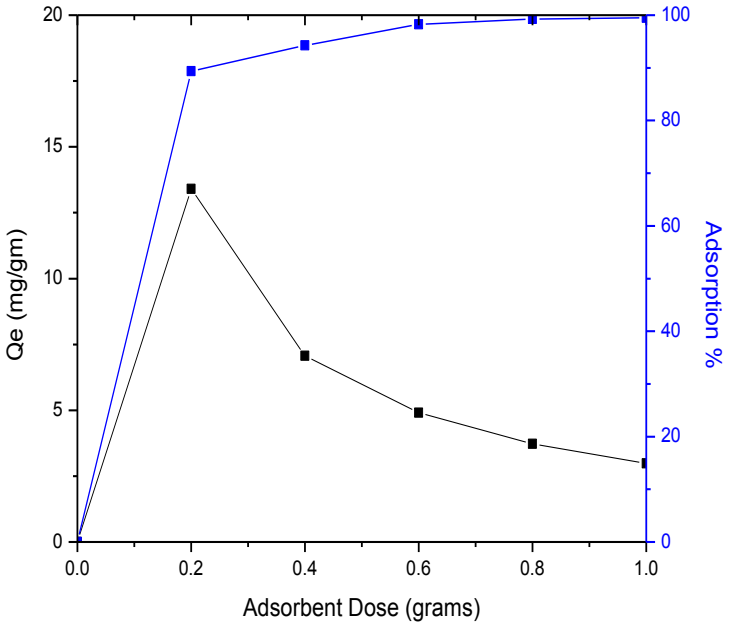
(Figure-4.21) Effect of pH on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of biomass (CS with Molecular Sieve Catalyst) AC:



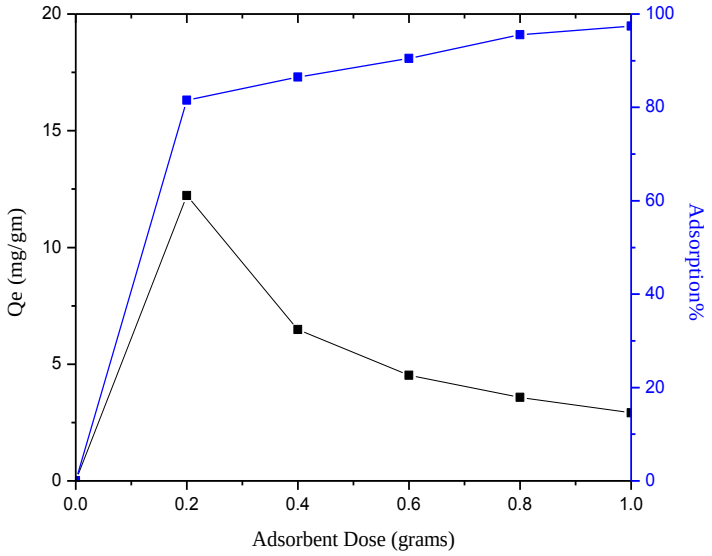
4.1.6.1.3 Effect of Adsorbent Dose:

The study of effect of adsorbent dose gives an idea of the effectiveness of an adsorbent and the ability of a dye to be adsorbed with a minimum dosage. From Figure-4.22-Figure-4.26 we observe that the amount of methylene blue adsorbed (Qe (mg/gm)) decreases from 13.404 (mg/gm) - 2.984(mg/gm) for tyre derived AC; from 12.22(mg/gm) – 2.92(mg/gm) for biomass (CS) AC; from 13.66 (mg/gm) – 2.974 (mg/gm) for biomass (CS with Zeolyte catalyst) AC; from 9.988 (mg/gm) – 2.915 (mg/gm) for biomass (CS with Bentonite catalyst) AC; from 12.789 (mg/gm) – 2.8621 (mg/gm) for biomass (CS with molecular sieve catalyst) AC. The decrease in amount of methylene blue adsorbed (Qe (mg/gm)) with the increase in adsorbent dosage is due to the split in the flux or the concentration gradient between the solute concentration in solution and the solute concentration in the surface of adsorbent. From the below figures we also observe that with increase in the adsorbent dosage the adsorption% of the methylene blue increases and reaches a maximum upto 99.467% for tyre derived AC; 97.43% for biomass (CS) AC; 99.150% for biomass (CS with Zeolyte catalyst) AC; 97.191% for biomass (CS with Bentonite catalyst) AC; 95.404% for biomass (CS with molecular sieve catalyst) AC. This increase in adsorption% is due to the availability of more binding sites as the dose of adsorbent increases. However the removal will grow upto certain limit and then remain constant, the limit in each case being still related to the effect of adsorbent on adsorption.

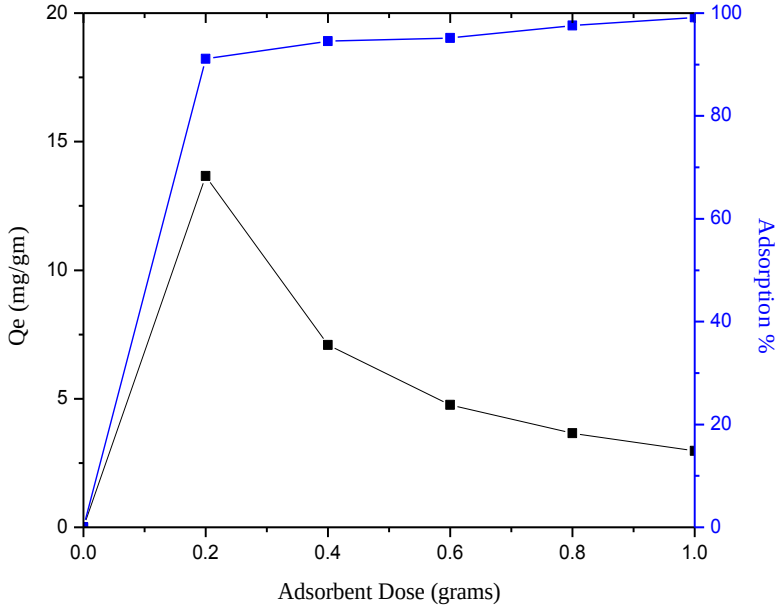
(Figure-4.22) Effect of adsorbent dose on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of tyre derived AC:



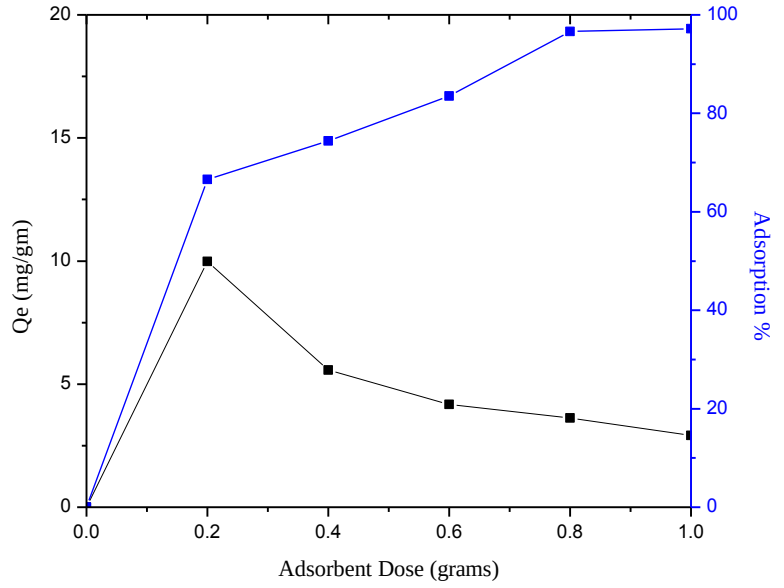
(Figure-4.23) Effect of adsorbent dose on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of biomass (CS) AC:



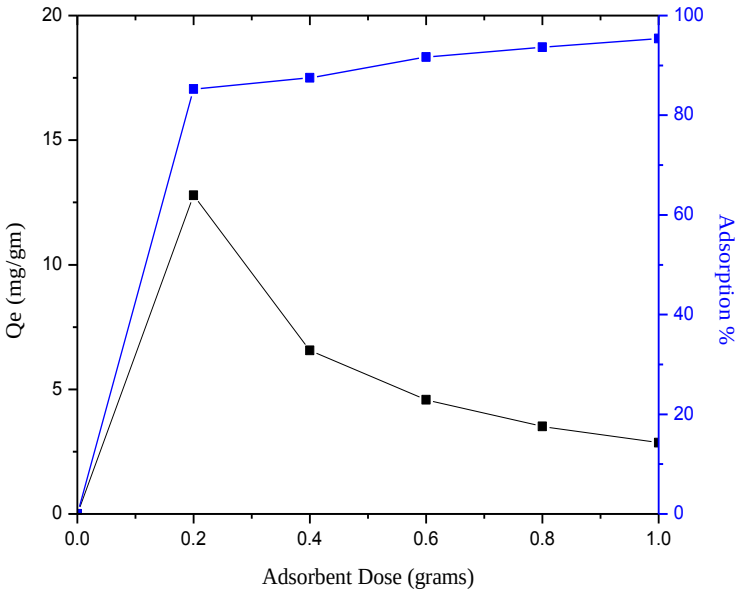
(Figure-4.24) Effect of adsorbent dose on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of biomass (CS with Zeolite Catalyst) AC:



(Figure-4.25) Effect of adsorbent dose on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of biomass (CS withBentonite Catalyst) AC:



(Figure-4.26) Effect of adsorbent dose on the amount of methylene blue adsorbed (Qe (mg/gm)) and adsorption % of biomass (CS with Molecular Sieve Catalyst) AC:



4.1.7: Adsorption Equilibrium Study:

The equilibrium adsorption isotherms were determined by plotting solid phase concentration (qe) against liquid phase concentration (Ce) of solute.

4.1.7.1: Langmuir Isotherm:

The Langmuir isotherm model is applicable to homogenous sorption where the sorption of each sorbate molecule on to the surface has equal sorption activation energy and is represented as follows.

$$\frac{1}{qe} = \frac{1}{Qo} + \left[\frac{1}{KQo}\frac{1}{Ce}\right]$$

The plots of 1/Ce versus 1/qe are linear which indicate that the adsorption data fitted reasonably to the Langmuir isotherm (*Figure – 4.27*). The constants were evaluated from the slope 1/KQo and intercept 1/Qo, (where Qo = K/a). The Langmuir constants obtained for all the adsorbents are summarized in Table-4.8. The adsorption data of the adsorbents were well fitted to Langmuir

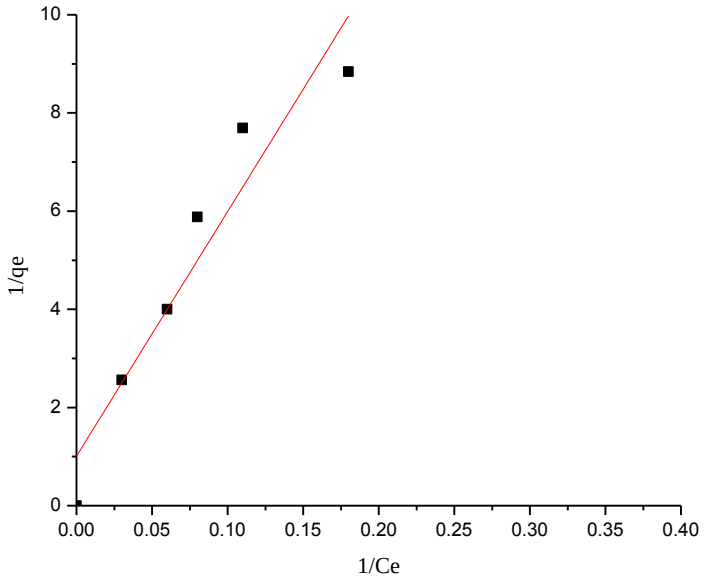
equation, essential characteristics of Langmuir isotherm can be explained in terms of dimensionless constant, separation factor (R) which is represented as

$$R = \frac{1}{1+aCi}$$

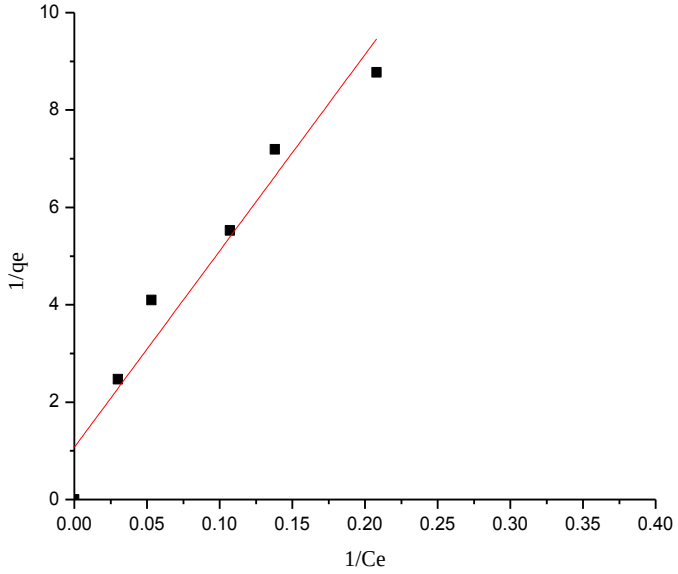
The value of R, a positive number (0 < R < 1), signifies the feasibility of the adsorption process for all developed ACs.

Figure-4.27: Langmuir Isotherms of ACs prepared for Methylene Blue Adsorption:

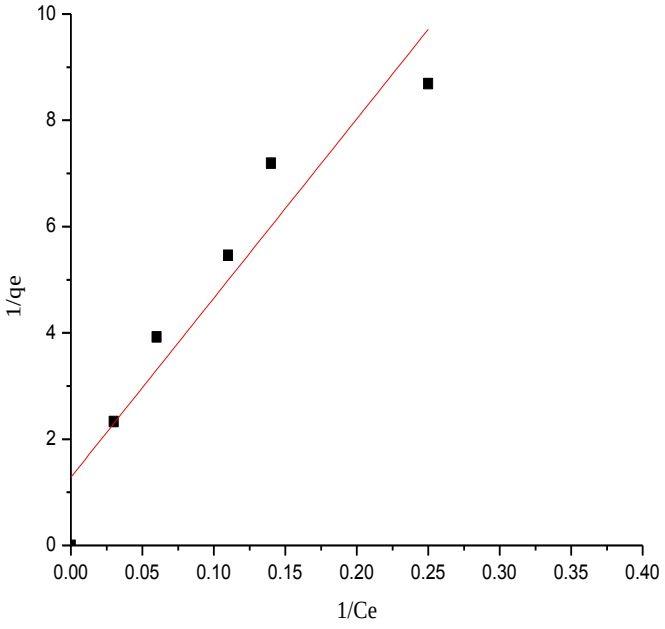
(Figure-4.27$_a$) Tyre derived AC:



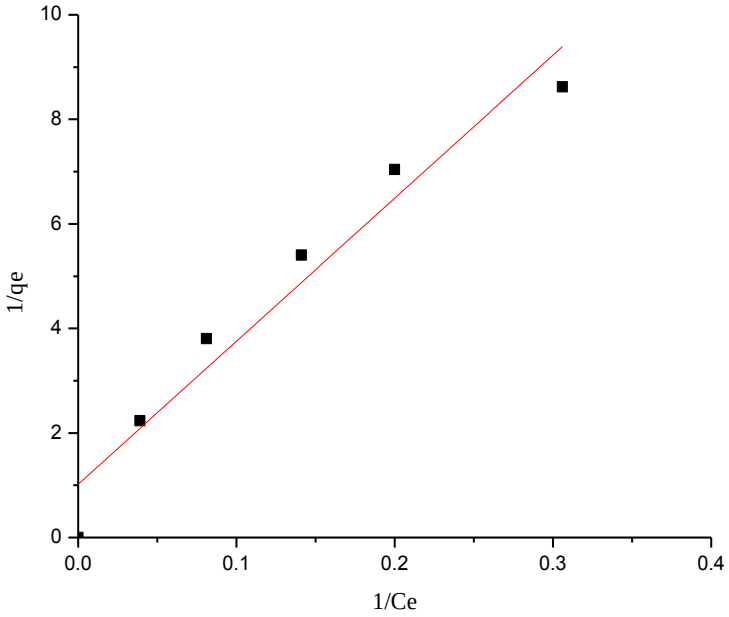
(Figure-4.27$_b$) Biomass (CS) AC:



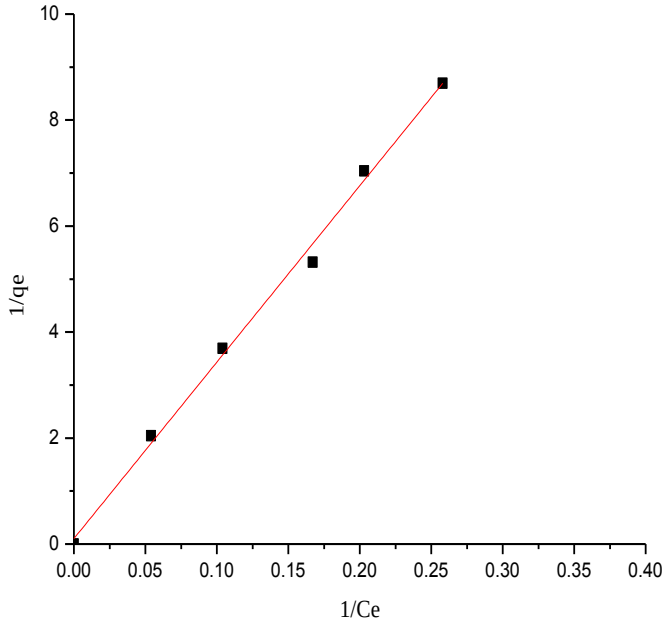
(Figure-4.27$_c$) Biomass (CS with Zeolite Catalyst) AC:



(Figure-4.27$_e$) Biomass (CS with Bentonite Catalyst) AC:



(Figure-4.27$_e$) Biomass (CS with Molecular Sieve Catalyst) AC:



4.1.7.2: Freundlich Isotherm:

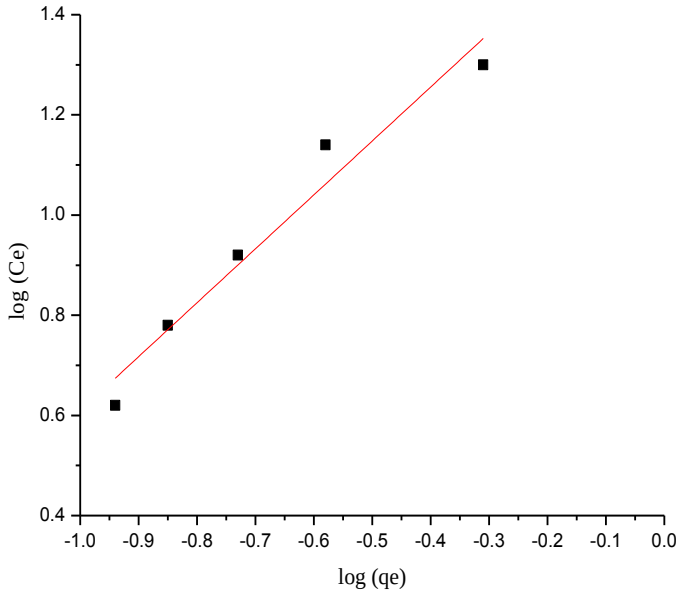
Freundlich isotherm which is characterized by the heterogeneity factor 1/n and is represented by the equation

$\log (q_e) = \log (K_f) + 1/n (\log (C_e)$

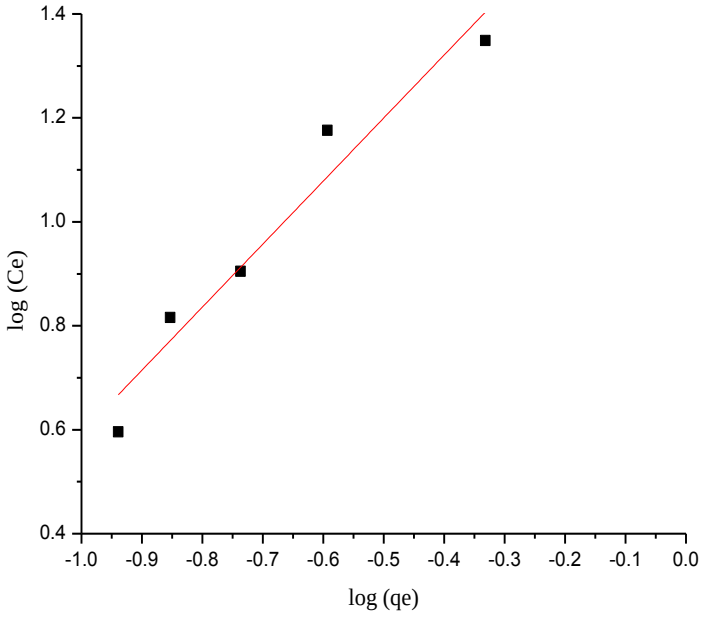
Where the intercept log (K_f) is the measure of adsorption capacity, and the slope 1/n is the adsorption intensity. The values of K_f and n were calculated from the intercept and slope of the plot of log (q_e) versus log (C_e) (*Figure-4.28*). The magnitude of n gives an indication on favorability of adsorption. It is generally stated that the value of n in the range of 2 – 10 represents good adsorption capacity, 1 – 2 moderately good, and less than 1 poor adsorption characteristics.

Figure-4.28: Freundlich Isotherms of ACs prepared for Methylene Blue Adsorption:

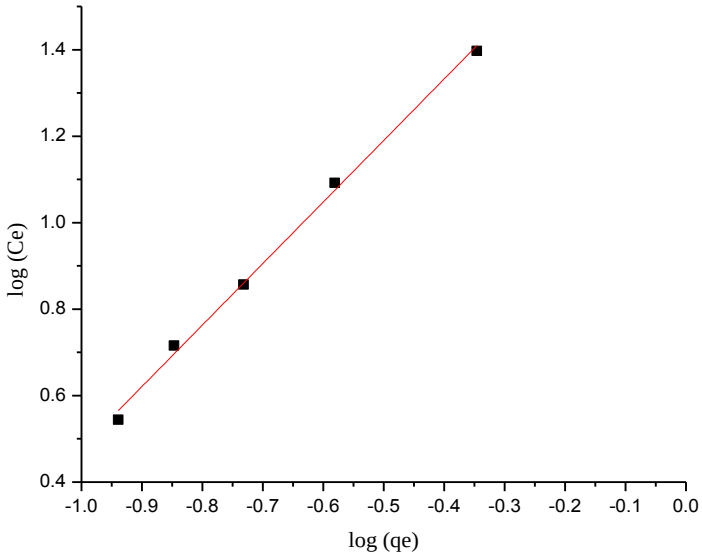
(Figure-4.28$_a$) Tyre derived AC:



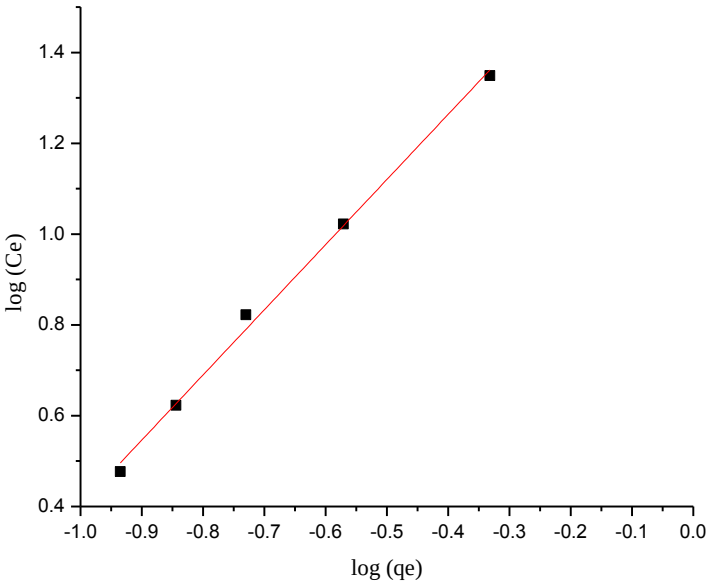
(Figure-4.28$_b$) Biomass (CS) AC:



(Figure-4.28$_c$) Biomass (CS with Zeolite Catalyst) AC:



(Figure-4.28$_d$) Biomass (CS with Bentonite Catalyst) AC:



(Figure-4.28$_e$) Biomass (CS with Molecular Sieve Catalyst) AC:

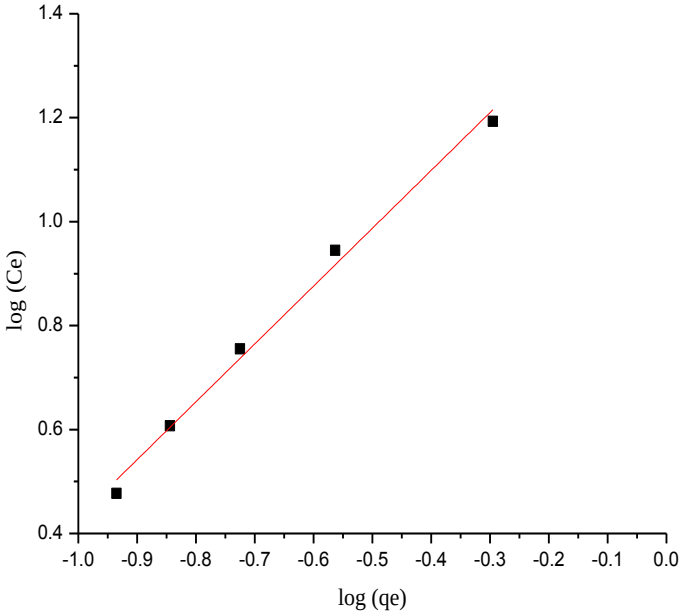


Table- 4.8: Langmuir and Freundlich isotherm constants for methylene blue adsorption on prepared AC:

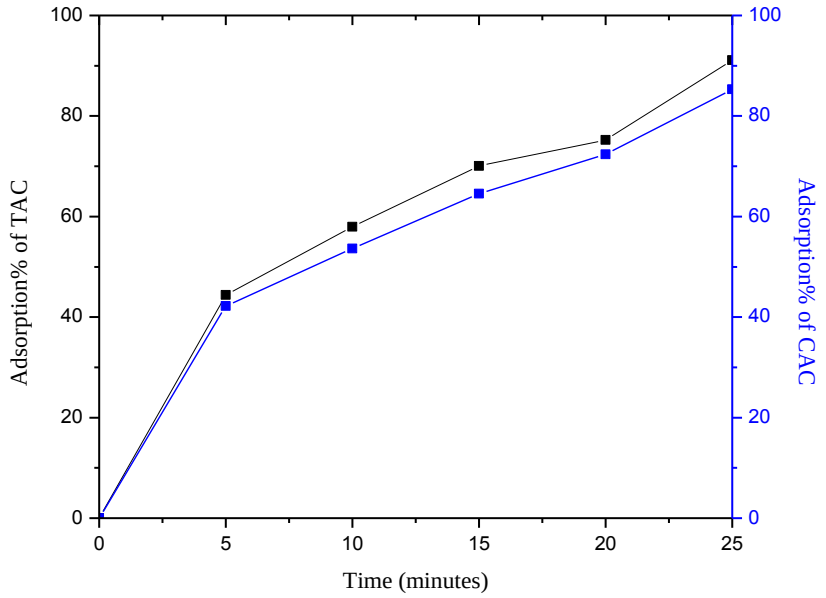
Isotherm Parameters	Tyre derived AC	Biomass (CS) AC	Biomass (CS with Zeolite catalyst) AC	Biomass (CS with Bentonite catalyst) AC	Biomass (CS with Molecular Sieve catalyst) AC
Langmuir K	0.375	0.183	0.39	0.273	0.031
Q_o	0.16	0.24	0.18	0.245	1.062
A	2.34	0.76	2.17	1.11	0.029
R	$4.25x10^{-3}$	0.0129	$4.58x10^{-3}$	$8.92x10^{-3}$	0.25
Freundlich K_f	$9.04x10^{-3}$	0.067	0.058	0.014	0.053
n	0.56	2.56	0.535	0.623	0.074

4.1.8: Comparison of Commercial AC and Rice Husk Carbon (RHC) with AC Prepared:

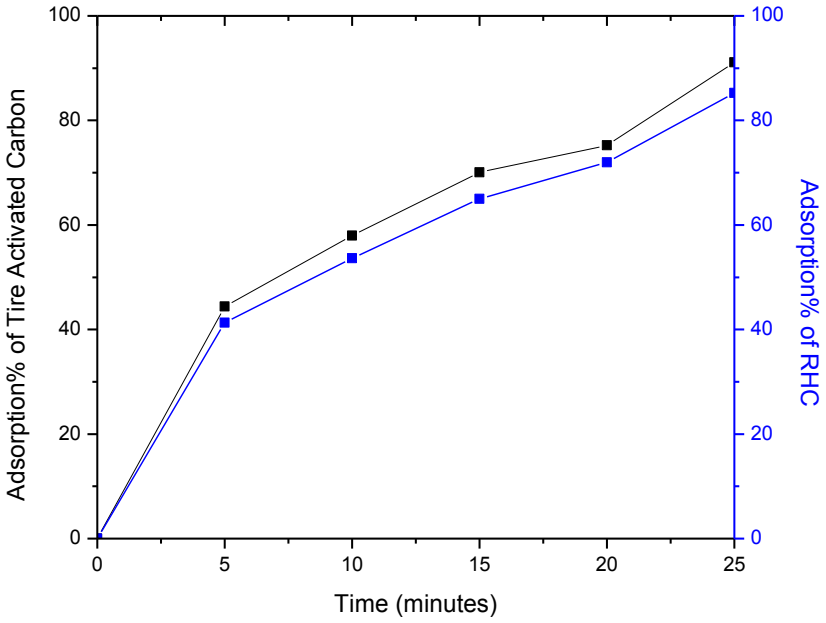
AC prepared from tyre and biomass (CS) char was compared with commercial AC (CAC) and rice husk carbon (RHC). Commercial AC and RHC was applied for the methylene blue removal from aqueous solution for comparative studies. From Figure-4.29 we observe that the adsorption % of AC prepared is more when compared to commercial AC. This is due to the presence of a higher surface area of prepared AC than commercial AC (CAC).

Figure-4.29: Comparison of Commercial AC (CAC) and RHC with AC prepared:

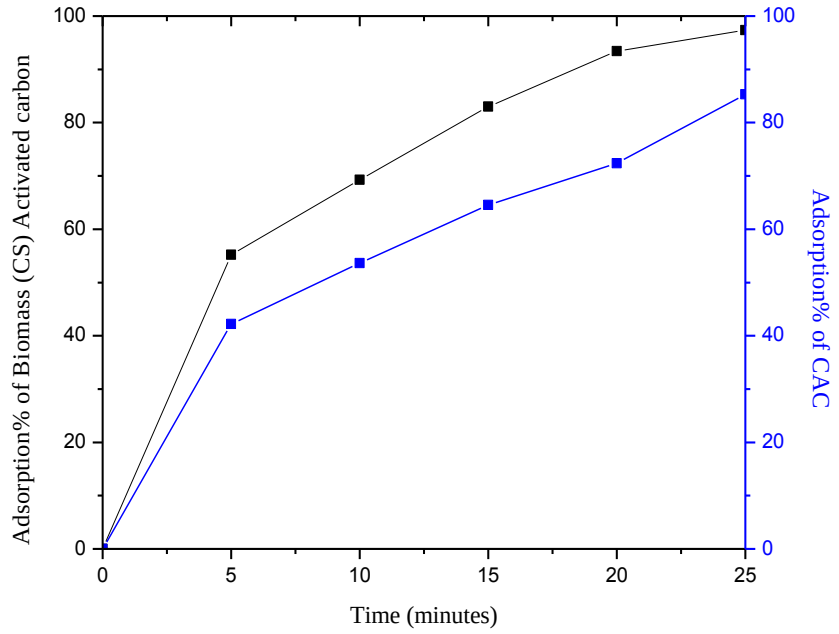
(Figure-4.29$_a$) CAC vs. TAC:



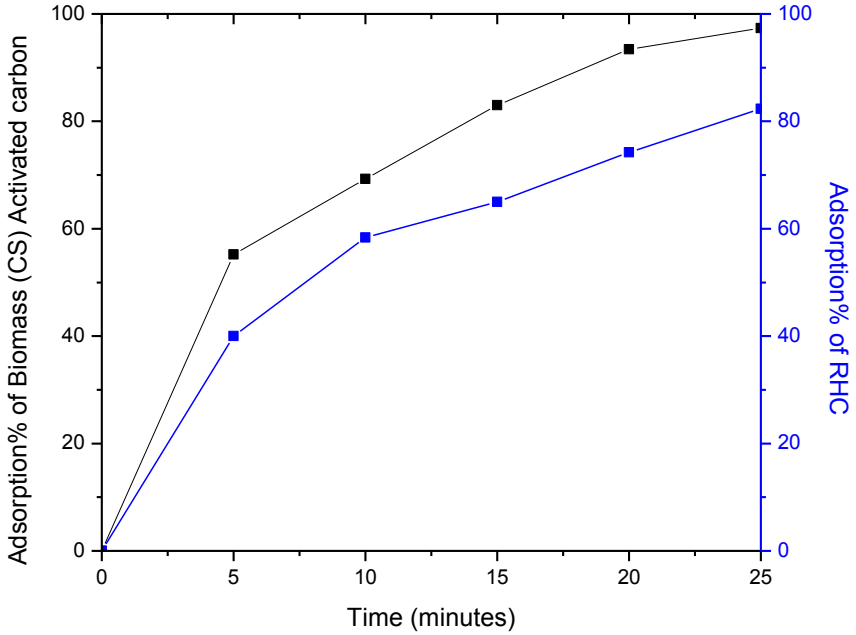
(Figure-4.29$_b$) RHC vs TAC:



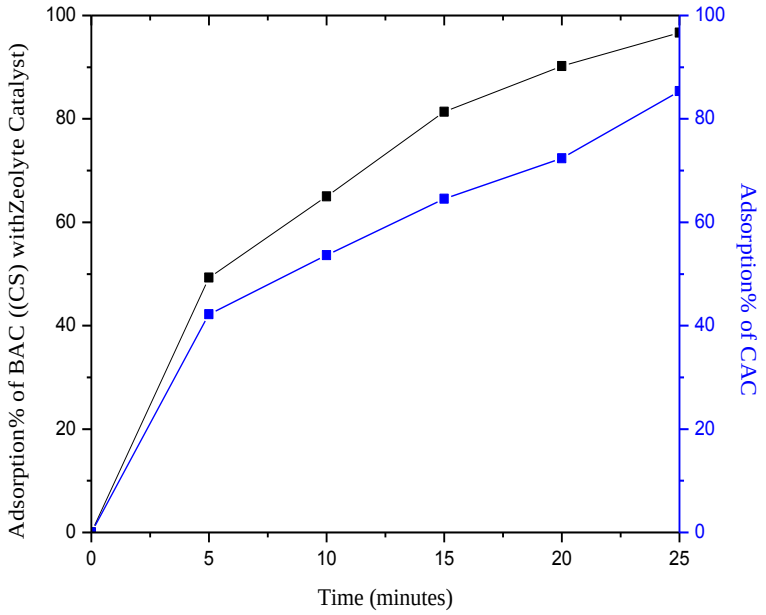
(Figure-4.29$_c$) CAC vs. BAC (CS):



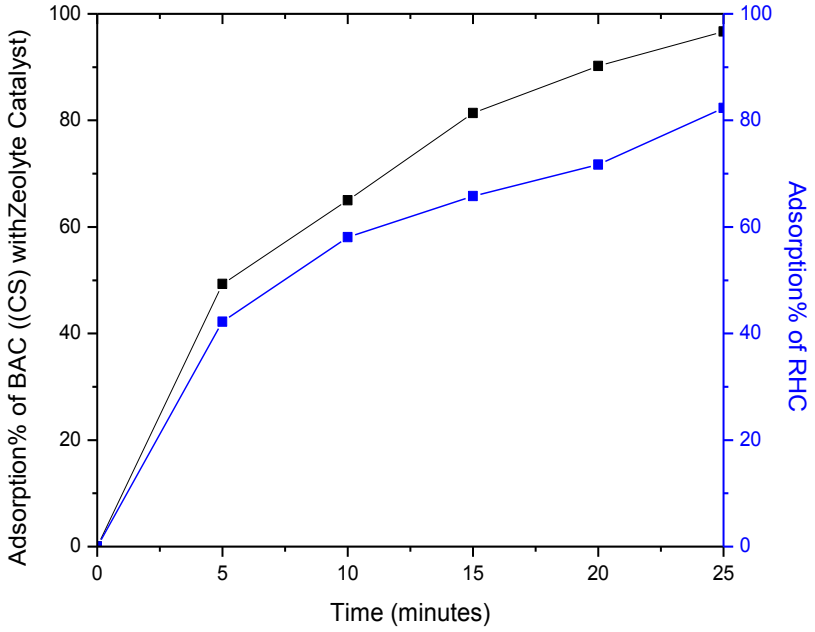
(Figure-4.29$_d$) RHC vs. BAC (CS):



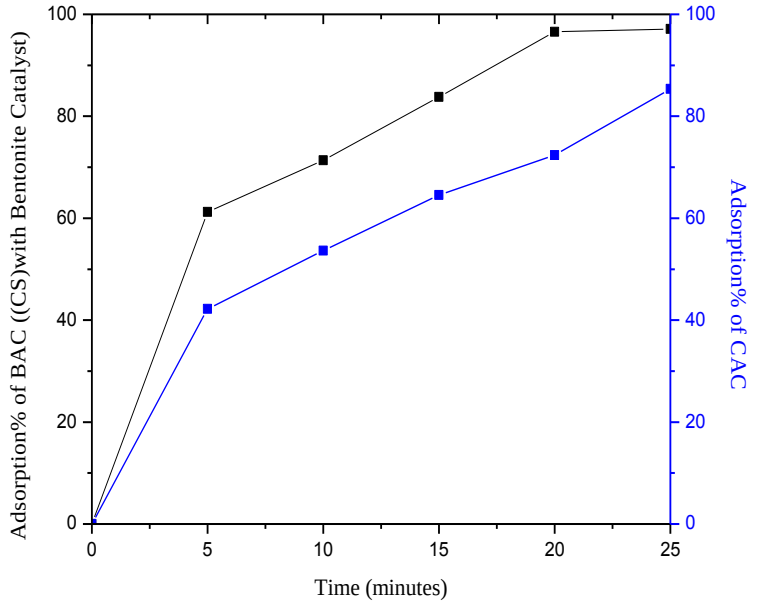
(Figure-4.29$_e$) CAC vs. BAC ((CS) with Zeolite Catalyst):



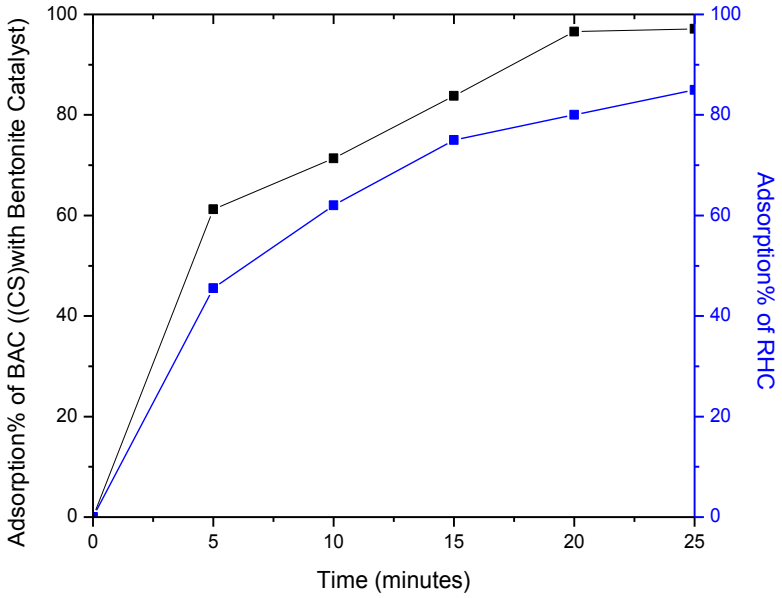
(Figure-4.29$_f$) RHC vs. BAC ((CS) with Zeolite Catalyst):



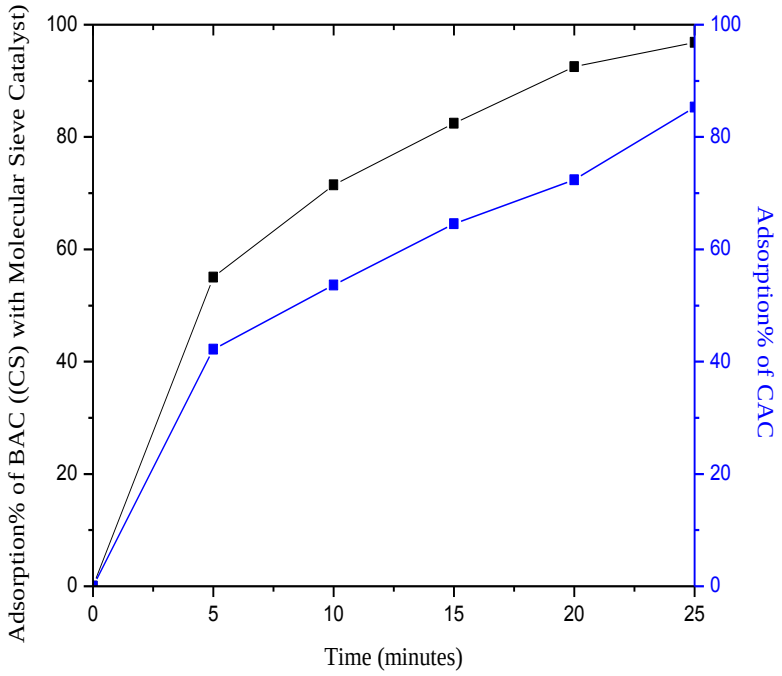
(Figure-4.29$_g$) CAC vs. BAC ((CS) with Bentonite Catalyst):



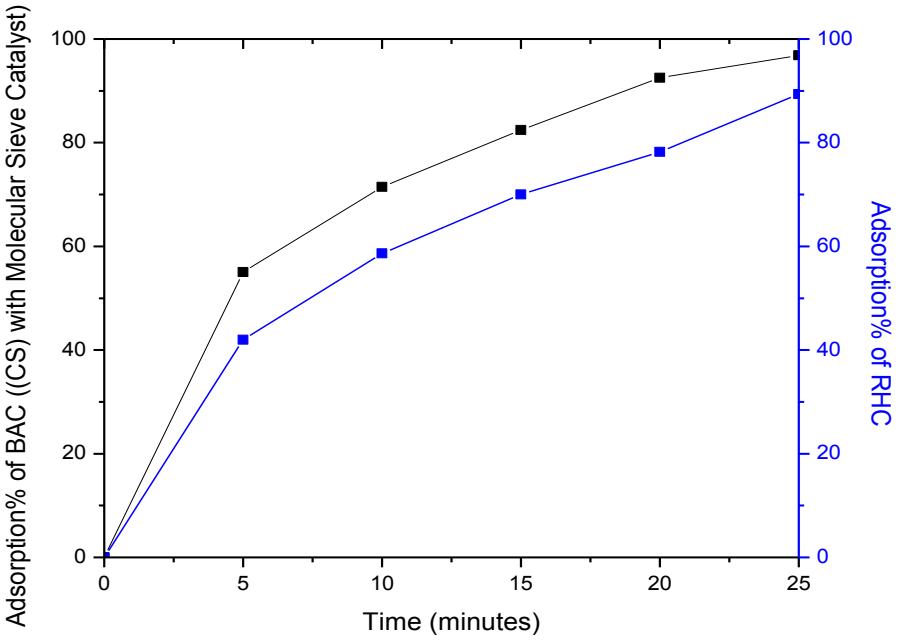
(Figure-4.29$_h$) RHC vs. BAC ((CS) with Bentonite Catalyst):



(Figure-4.29$_i$) CAC vs. BAC ((CS) with Molecular Sieve Catalyst):



(Figure-4.29$_j$) RHC vs. BAC ((CS) with Molecular Sieve Catalyst):



Chapter-5

Conclusions and Future Scope

5.0 Summary:

The objective of the experimental study is prepare and characterize AC from tire and biomass (castor seed with different catalysts) char. It also aimed at estimating the methylene blue adsorption capacity of the developed AC and to compare it with the commercial AC in aqueous phase adsorption. AC with high surface area was developed for this purpose.

5.1 Conclusions:

Based on the detailed experimental investigation the conclusions derived are as follows:

ACs with high surface area are prepared by chemical activation method using tyre and biomass (CS) char as precursors. Maximum surface area of 382.9 m^2/gm for tyre derived AC; 475.96 m^2/gm for biomass (CS) AC; 499.33 m^2/gm for biomass (CS with zeolite catalyst) AC; 449.22 m^2/gm for biomass (CS with bentonite catalyst) AC; 453.45m^2/gm for biomass (CS with molecular sieve catalyst) AC, are observed. Adsorption of methylene blue on acid treated AC has been investigated by using UV-Visible spectrophotometer at a wavelength of 660nm. On comparison of adsorption% of prepared ACs we observe that AC prepared from biomass (CS) has more adsorption% of 97.335%. Freundlich adsorption isotherm show the good adsorption capacity to adsorption data for biomass (CS) AC (n=2.56). On comparison with commercial AC and RHC the AC prepared from precursor selected shows more adsorption%, this is due to the presence of a higher surface area of prepared AC than commercial AC.

5.2 Future Work:

- Preparation of AC can be done by physical activation process also (two stage activation and microwave heating etc) and can be compared with the results obtained by chemical activation.
- Utilization of AC for the removal of various organic and inorganic pollutants present in water can be done.
- Adsorption kinetic study of prepared AC can be done by using pseudo first and second order kinetic model.
- Regeneration of AC can be done by using hot water and mild acid.

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Publications

Journal:

1. **A.V.S.L.Sai Bharadwaj**, R.K. Singh. Utilization of Waste Tire Char and Its Applications in Liquid-Phase Adsorption: A review. International Journal of Advance Chemical Science and Applications, Volume-1 Issue-2 (2014); ISSN (print: 2347-7601), ISSN (online: 2347-761X).
2. **A.V.S.L.Sai Bharadwaj**, R.K. Singh. Preparation and Characterization of Activated Carbon Prepared from Waste Tire Char and Its Applications in Liquid-Phase Adsorption. Environment Observer, Volume-21 (2014); ISSN (2320-5997).

Conferences:

1. **A.V.S.L.Sai Bharadwaj**, R.K. Singh. Utilization of Waste Tire Char and Its Application in Liquid-Phase Adsorption: A review. 3rd International Conference on Engineering and Technology (ICET-2014), 11th May 2014 held at Bangalore.
2. **A.V.S.L.Sai Bharadwaj**, R.K. Singh. Preparation and Characterization of Activated Carbon Prepared from Waste Tire Char and Its Applications in Liquid-Phase Adsorption. 2nd International Conference on Waste Water Technology for Greening India, 29th June 2014 held at College of Engineering-Pune.
3. **A.V.S.L.Sai Bharadwaj**, R.K. Singh. Characterization of Waste Tire Char and Its Application in Waste Water Treatment: A review. National Conference on Recent Trends in Chemical Engineering (RTCE-2014), 25-26 February 2014 held at Anna University Chennai.